PB87-145355

# Field Evaluation of Methodology for Measurement of Cadmium in Stationary Source Stack Gases

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-145355

EPA/600/4-86/048
December 1986

# FIELD EVALUATION OF METHODOLOGY FOR MEASUREMENT OF CADMIUM IN STATIONARY SOURCE STACK GASES

by

R. F. Moseman, D. B. Bath, J. R. McReynolds,
D. J. Holder, and A. L. Sykes
Radian Corporation
3200 East Chapel Hill Road/Nelson Highway
Post Office Box 13000
Research Triangle Park, North Carolina 27709

T. E. Ward
Quality Assurance Division
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

EPA Contract No. 68-02-4119
Work Assignment Nos. 14 and 21

Project Officer

Thomas E. Ward
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA/600/4-86/048 | | PB87 145355/AS |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| FIELD EVALUATION OF METHODOLOGY FOR MEASUREMENT OF CADMIUM IN STATIONARY SOURCE STACK GASES | December 1986 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| R.F. Moseman, D.B. Bath, J.R. McReynolds, D.J. Holder, A.L. Sykes, T.E. Ward | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| Radian Corporation<br>3200 East Chapel Hill Road<br>Research Triangle Park, NC 27711 | 11. CONTRACT/GRANT NO.<br>68-02-4119 |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| U.S. Environmental Protection Agency<br>Office of Research and Development<br>Environmental Monitoring Systems Laboratory-RTP<br>Research Triangle Park, NC 27711 | Final<br>14. SPONSORING AGENCY CODE<br>EPA-600 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A laboratory and field evaluation study was done to develop methodology for the measurement of cadmium in stationary source stack emissions. Field evaluations were performed at a municipal solid waste incinerator and a sewage sludge incinerator. The methodology was tested through the laboratory and field sampling validation phases to evaluate precision and accuracy of the proposed method. Colocated, quadruplicate flue gas samples of nominally 30 and 60 dscf in 1 and 2 hours sampling time were collected to assure an adequate cadmium content, a representative sample, and the production of data to validate the method in terms of between-train precision. The overall accuracy and precision of the analysis procedure were 89.2 percent and 1.7 percent, respectively. The detection limit of the atomic absorption instrument was 0.03 ug/mL. The method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample was found to be 0.05 to 0.025 ug Cd, respectively per dscf (1.7 to 0.88 ug Cd per dscm). The percent coefficient of variation (precision) of between-train cadmium concentrations averaged 13.5% at the municipal incinerator and 3.8% at the sewage sludge incinerator. Separate analyses of the front half (probe and filter) and back half (impingers) of the field samples revealed that 99.9% of the cadmium was collected in the front half. The methodology proved to be a reliable sampling approach to determine cadmium emissions from the stationary sources tested.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Emission Measurement of Cadmium<br>Cadmium Stationary Source Measurement<br>Emission Measurement Methods, Cadmium Stationary Sources<br>Source Emission Measurement, Cadmium | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| Release to Public | Unclassified | 132 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | Unclassified | |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER NOTICE

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under contract number 68-02-4119 to Radian Corporation. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

## FOREWARD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Cadmium emissions are being studied by the Agency for environmental effects. Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for the quantification of cadmium emissions from stationary sources.

John C. Puzak
Deputy Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

## ABSTRACT

An initial laboratory and field evaluation study was done to assess the usefulness of a Modified EPA Method 5 sampling train and flame atomic absorption spectrometry for the measurement of cadmium in stationary source stack emissions. Field evaluations were performed at a municipal solid waste incinerator and a sewage sludge incinerator. These industrial sources are currently being evaluated by EPA/OAQPS for multiple pollutants including cadmium emissions. Also, this methodology is being developed for application, subject to verification, at other sources of cadmium emissions at or above the method detection limit. A formulation of the methodology was tested through the laboratory and field sampling validation phases to evaluate precision and accuracy of the proposed method. Colocated, quadruplicate flue gas samples of nominally 30 and 60 dscf in 1 and 2 hours sampling time were collected to assure an adequate cadmium content, a representative sample (including volume of stack gas and duration of sampling time), and the production of data to validate the method in terms of between-train precision. The overall accuracy and precision of the analysis procedure were 89.2 percent and 1.7 percent, respectively. The method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample was found to be 0.05 to 0.025 ug Cd, respectively per dscf (1.7 to 0.88 ug Cd per dscm). The detection limit of the atomic absorption instrument was 0.03 ug/mL. The percent coefficient of variation (precision) of between-train cadmium concentrations averaged 13.5% for the six sampling runs conducted at the municipal solid waste incinerator (field test #1). The precision of between-train cadmium concentrations averaged 3.8% for the four sampling runs conducted at the sewage sludge incinerator (field test #2). Separate analyses of the front half (probe and filter) and back half (impingers) of the field samples revealed that all of the cadmium was collected in the front half, with the exception of one sample. In this sample, a faulty filter leaked and a small percentage

of the cadmium was captured in the impingers. In all of the other impinger samples, the cadmium concentration was below the detection limit. Precision of the cadmium results was not affected by varying the sample size from 30 to 60 dscf.

CONTENTS


| | Page |
|---|---|
| Disclaimer | ii |
| Foreward | iii |
| Abstract | iv |
| Figures | vii |
| Tables | viii |
| Glossary of Terms | ix |
| Acknowledgements | x |
| 1 Introduction | 1 |
| 2 Conclusions | 3 |
| 3 Recommendations | 5 |
| 4 Method Formulation and Design of Evaluation Studies | 6 |
| 5 Results of the Laboratory Evaluations | 9 |
| Calibration Curve Precision | 9 |
| Analytical Precision and Accuracy Comparisons of AAS, ICAP and NAA | 10 |
| Blank Determinations | 12 |
| Field Sample Analyses | 12 |
| Recommendations for Future Analyses | 16 |
| 6 Results of the Field Evaluation | 19 |
| Process Description | 20 |
| Sampling Location and Apparatus | 24 |
| Experimental Design and Sample Collection | 29 |
| Train and Reagent Blanks | 29 |
| Analytical Results and Discussion | 35 |
| 7 Quality Assurance and Quality Control | 43 |
| QA Program Objectives | 43 |
| Summary of QA/QC Activities | 43 |
| References | 53 |
| Appendices | |
| A. Quality Assurance and Site Specific Project Plan | 54 |
| B. Procedures Used to Assess Data Precision and Accuracy | 85 |
| C. Site Secific Systems Audit Checklist | 95 |
| D. Field Test Program Data | 106 |

CONTENTS


| | Page |
|---|---|
| Disclaimer | ii |
| Foreward | iii |
| Abstract | iv |
| Figures | vii |
| Tables | viii |
| Glossary of Terms | ix |
| Acknowledgements | x |
| 1 Introduction | 1 |
| 2 Conclusions | 3 |
| 3 Recommendations | 5 |
| 4 Method Formulation and Design of Evaluation Studies | 6 |
| 5 Results of the Laboratory Evaluations | 9 |
| Calibration Curve Precision | 9 |
| Analytical Precision and Accuracy Comparisons of AAS, ICAP and NAA | 10 |
| Blank Determinations | 12 |
| Field Sample Analyses | 12 |
| Recommendations for Future Analyses | 16 |
| 6 Results of the Field Evaluation | 19 |
| Process Description | 20 |
| Sampling Location and Apparatus | 24 |
| Experimental Design and Sample Collection | 29 |
| Train and Reagent Blanks | 29 |
| Analytical Results and Discussion | 35 |
| 7 Quality Assurance and Quality Control | 43 |
| QA Program Objectives | 43 |
| Summary of QA/QC Activities | 43 |
| References | 53 |
| Appendices | |
| A. Quality Assurance and Site Specific Project Plan | 54 |
| B. Procedures Used to Assess Data Precision and Accuracy | 85 |
| C. Site Secific Systems Audit Checklist | 95 |
| D. Field Test Program Data | 106 |

FIGURES


| Number | | Page |
|---|---|---|
| 1 | Analysis of NBS urban particulate | 13 |
| 2 | Analysis of urban particulate | 14 |
| 3 | Representative atomic absorption spectrometry calibration curve for cadmium | 17 |
| 4 | Sewage sludge treatment plant schematic flow diagram | 21 |
| 5 | Sampling location - side view | 25 |
| 6 | Sampling location - top view (including the quad train) | 26 |
| 7 | Sampling location for field test #1 - velocity profile | 27 |
| 8 | Sampling location for field test #2 - velocity profile | 28 |
| 9 | Quad train configuration method as used during cadmium validation test | 30 |
| 10 | Quad probe sampling nozzle configuration | 31 |
| 11 | MM5 cadmium sampling train | 32 |

TABLES


| Number | | Page |
|---|---|---|
| 1 | Accuracy and Precision of Cadmium in NBS Standard Reference Material #1648, Urban Particulate | 11 |
| 2 | Blank Filter Determinations for Cadmium | 15 |
| 3 | Expected Range of Cadmium Concentrations for Various Cadmium Source Categories | 18 |
| 4 | Plant Production Data for Field Test #1 | 22 |
| 5 | Plant Production Data for Field Test #2 | 23 |
| 6 | Test Configuration for the First Cadmium Sampling Field Test | 33 |
| 7 | Test Configuration for the Second Cadmium Sampling Field Test | 34 |
| 8 | Cadmium Concentrations and Within-Run Precision Assessments for Field Test #1 | 36 |
| 9 | Cadmium Concentrations and Within-Run Precision Assessments for Field Test #2 | 37 |
| 10 | Comparison of Field Test #1 Cadmium Concentrations, Particulate Concentration, Cadmium to Particulate Concentration, and Isokinetic Rates for Each Run | 39 |
| 11 | Comparison of Field Test #2 Cadmium Concentrations, Particulate Concentration, Cadmium to Particulate Concentration, and Isokinetic Rates for Each Run | 41 |
| 12 | Cadmium Glassware Precleaning Procedure for the Field Tests | 45 |
| 13 | Field Test #1 Analytical Results for Cadmium Modified EPA Method 5 Field Blanks Using AAS | 46 |
| 14 | Field Test #2 Analytical Results for Cadmium Modified EPA Method 5 Field Blanks Using AAS | 47 |
| 15 | Summary of Field Test #1 Isokinetic Calculations and Leak Check Results for the Modified EPA Method 5 Cadmium Sampling | 49 |
| 16 | Summary of Field Test #2 Isokinetic Calculations and Leak Check Results for the Modified EPA Method 5 Cadmium Sampling | 50 |
| 17 | Summary of Cadmium Analytical Quality Control Checks | 51 |

## GLOSSARY OF TERMS

| | |
|---|---|
| AAS | Atomic Absorption Spectrometry |
| C | Centigrade |
| Cd | Cadmium |
| CC | Correlation Coefficient |
| CV | Coefficient of Variation |
| DSCF | Dry Standard Cubic Feet |
| DSCFM | Dry Standard Cubic Feet Per Minute |
| DSCM | Dry Standard Cubic Meters |
| EMSL | Environmental Monitoring Systems Laboratory |
| EPA | Environmental Protection Agency |
| ESP | Electrostatic Precipitator |
| F | Fahrenheit |
| ICAP | Inductively Coupled Argon Plasma Spectroscopy |
| MM5 | Modified EPA Method 5 |
| mg | Milligram |
| mL | Milliliter |
| NAA | Neutron Activation Analysis |
| NBS | National Bureau of Standards |
| QA | Quality Assurance |
| QC | Quality Control |
| s | Standard Deviation |
| SASS | Source Assessment Sampling System |
| SRM | Standard Reference Material |
| ug | Microgram |

## ACKNOWLEDGEMENTS

Radian Corporation, Research Triangle Park, North Carolina, conducted this work under Contract No. 68-02-4119 for the Quality Assurance Division, Environmental Monitoring Systems Laboratory of the U.S. Environmental Protection Agency. Dr. Robert McAllister contributed to the statistical treatment of the data, and Esther Robb and Mark Dow performed sample preparation and analyses. Michael Hartman and Andrew Miles assisted in organization of the field test data acquired by Messrs. Gary Henry, Lee Garcia, William Gergen, and Ms. Dorie Holliman. Cooperation of the emission source personnel is appreciated. M. Rodney Midgett and Thomas J. Logan gave helpful advice and comments throughout the project. All of the above contributions are gratefully acknowledged.

# SECTION 1

# INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is currently investigating cadmium emissions from stationary sources as a potentially hazardous air pollutant. In the event that EPA makes a determination to regulate cadmium emissions, appropriate methods of sampling and analysis must be available to quantify accurately the emission of cadmium in stack gases from stationary sources.

The Environmental Monitoring Systems Laboratory (EMSL) of EPA located in Research Triangle Park, North Carolina is performing development and validation of a methodology for sampling and analysis of cadmium emissions. The purpose of this report is to present the results of field and laboratory studies funded by EPA and conducted by Radian Corporation. The objectives of the study were as follows:

- Determine the applicability of a Modified EPA Method 5 train and flame atomic absorption spectrometry for the measurement of stationary source stack gas cadmium.
- Evaluate the precision and accuracy of the proposed laboratory analytical technique. The technique consists of sample preparation followed by analysis for cadmium using atomic absorption spectrometry.
- Assure that the method has a detection limit sufficient to measure expected cadmium in municipal solid waste and sewage sludge incinerator flue gas samples of nominally 30 to 60 dry standard cubic feet.
- Combine the results of these determinations to validate the proposed sampling and analytical methodologies.

The method validation was conducted in several stages. The initial effort focused on defining appropriate sampling and analytical procedures. The procedures that were chosen are discussed in Section 4. A laboratory study was then conducted to determine overall precision and accuracy of the analytical portion of the methodology including sample preparation and analysis. This work is summarized in Section 5 with supporting details in Appendices A and B. The next stage of this program involved a field evaluation conducted at a large municipal solid waste incinerator and a sewage sludge incinerator.

The field evaluations were conducted according to the procedures outlined in the site-specific Quality Assurance and Project Plans, hereafter referred to as the QA Plans. The procedures used to conduct the field evaluation and the results of the cadmium analyses done on the collected field samples, are summarized in Section 6. Sections 2 and 3 present the conclusions and recommendations from this overall effort.

## SECTION 2

## CONCLUSIONS

The quantification of cadmium in stationary source stack gases consists of two portions: sample collection and laboratory analysis. The precision of the sample collection procedures was evaluated by comparing the cadmium concentrations of samples collected using concurrent quad Modified EPA Method 5 (MM5) sampling trains. The accuracy and precision of the analytical procedures, including the sample preparation steps, were evaluated by performing replicate analyses on known amounts of cadmium to determine the percent recovery and repeatability of the method. Based on this work, the following conclusions can be made:

- A Modified EPA Method 5 sampling train and flame atomic absorption spectrometry were found to be applicable for the measurement of cadmium in stationary stack gas samples.
- The overall accuracy and precision of the analytical steps were 89.2 percent and 1.7 percent, respectively. The detection limit of the analytical instrument was 0.03 ug Cd/ml of prepared sample.
- During analysis of the samples from field test #2, an NBS SRM urban particulate sample was analyzed and recovery was found to be 95 percent.
- The corresponding method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample is 0.05 and 0.025 ug Cd/dscf (1.7 and 0.88 ug Cd/dscm). The determined levels of cadmium at the sources tested ranged from 32 to over 1000 ug/dscm.

The percent coefficient of variation (CV) of between-train cadmium concentrations ranged from 3.4 to 23.1% for the six sampling runs conducted during field test #1, and ranged from 2.8 to 4.7%, for field test #2. The pooled CVs were 13.5% and 3.8% for field tests 1 and 2, respectively. The method bias was not affected by total sample volume. Stack gas samples of approximately 30 to 60 dscf were collected, and the cadmium results for the two sample sizes did not differ significantly for either field test. Greater than 99.9 percent of the cadmium was collected in the front half of the sampling train for each run. There was one exception to this in which a faulty filter leaked, however, even in this one train 97% of the cadmium was captured in the front half and only 3% in the impingers. Since greater than 99.9 percent of the cadmium was collected in the front half in these type tests a strong case exists to delete the back half analysis and to use water instead of the dilute $HNO_3$ solution in the impingers. Thus, the combined results of the method evaluation indicate that the proposed sampling and analysis methodologies are suitable for the measurement of cadmium in stack gases of these source categories.

## SECTION 3

## RECOMMENDATIONS

- A Modified EPA Method 5 sampling train and flame atomic absorption spectrometry are recommended for the measurement of cadmium in stationary stack gases.

- If a purchased stock solution of cadmium is used for preparation of working standards, the concentration should be verified against an independently prepared cadmium standard.

- At least one analysis sample from each source should be checked using the method of additions to ascertain that the chemical composition and physical properties of the sample do not cause erroneous analytical results.

- Analysis for cadmium of the impinger solutions (back half) of the sampling train at municipal and sewage sludge incinerators may be omitted when conditions of testing are not significantly different from those described in this report. When impinger solution (back half) analysis for cadmium is not performed, water as in Method 5 may be used in the impingers instead of dilute $HNO_3$.

## SECTION 4

## METHOD FORMULATION AND DESIGN OF EVALUATION STUDIES

The sampling and analytical methods evaluated in this field and laboratory study were proposed after a thorough literature search. Sampling methods[1,2], sample preparation techniques[3,4], and methods for analysis[5] of cadmium emissions from stationary sources were reviewed. The Source Assessment Sampling System (SASS) and EPA Method 5 sampling train were reviewed as possible sampling methods. The analytical methods under consideration included amperometric titration, voltammetry/polaragraphy, colorimetry, x-ray techniques, gamma and neutron activation, emission spectrography, mass spectrometry, inductively coupled argon plasma spectroscopy, and flame and flameless atomic absorption spectrometry. Possible sample preparation techniques included ultrasonic extraction and variations of acid digestion.

The various methods of sampling, sample preparation and analyses were then compared according to method detection limit, sensitivity, precision, speed, complexity, availability, cost, and overall practicality. After considering these factors and reviewing the literature, it was determined that sample collection using a modified EPA Method 5 sampling train, followed by acid digestion in a Parr Bomb and flame atomic absorption spectrometry would be used for the sampling and analysis of cadmium emissions from stationary sources.

The laboratory validation phase of this work was designed to assess the combined precision and accuracy of the sample preparation and analysis steps of the method using a National Bureau of Standards (NBS) urban particulate sample. Samples were digested using a mixture of nitric and hydrofluoric acids in a Parr bomb, and analyzed in quadruplicate using three different methods, including flame atomic absorption spectrophotometry (AAS), inductively-coupled argon plasma spectroscopy (ICAP) and neutron activation analysis (NAA).

A weighed amount of each particulate sample was digested along with a glass fiber filter to provide a background matrix consistent with the field samples. Following digestion, each sample was split for analysis by atomic absorption spectroscopy (AAS), neutron activation (NAA) and inductively coupled argon plasma spectroscopy (ICAP). The two additional analytical techniques were used to confirm the results obtained by AAS. Filter blanks were also digested and analyzed. The filter blanks were analyzed to determine the amount of cadmium present in the glass fiber filter and acid reagents.

The sampling portion of the study was designed to assess the efficiency of the glass fiber filter for collection of cadmium from stack gases. In previous work it was common to use from 0.1 N to 0.8 N (5%) nitric acid in water to attempt to capture and hold certain trace elements including cadmium in solutions through which stack aerosols were passed. The concentration of 5% nitric acid in water in the impingers was chosen for this research because it is reasonable to handle and because the level necessary could be determined best in field sampling. Impingers containing 5% nitric acid or distilled water (depending on the test run) were used in the MM5 trains downstream from the filter to trap any cadmium should any have passed through the filter. A quad-probe was used to permit the simultaneous collection of four samples from the same nominal point in the stack (co-located samples) by a single probe[6]. The precision of the sampling method was evaluated by determining the concentration of cadmium in each of the four samples.

Samples were collected isokinetically for periods of roughly one or two hours to yield total sample volumes ranging from 30 to 79 dscf. The sample volumes collected were chosen to demonstrate that: 1) cadmium emissions from a municipal solid waste incinerator and a sewage sludge incinerator could be measured in samples of 30 dscf, and 2) increasing the size of the sample volume (above 30 dscf) would not affect the analytical precision and accuracy of cadmium concentration results.

In order to recover all of the cadmium from the sampling train components, the front half rinses were combined with the glass fiber filter for digestion and analysis[7]. The impinger solutions and back half rinses were combined and analyzed to determine if cadmium was

captured in the back half of the MM5 train. At the direction of the EPA Technical Project Manager, the impingers in one of the six tests of field test #1 were filled with distilled water in place of 5% nitric acid to assess how well distilled water could catch breakthrough cadmium and to avoid the use of acid whenever possible. (All test #2 runs used 5% nitric acid.)

In addition to the analysis of field samples, several other analyses were performed as part of the laboratory validation procedures. Sample train component blanks (probes and nozzles) and reagent container blanks were analyzed using AAS to evaluate the quality control associated with the field sample preparation procedures.

## SECTION 5

## RESULTS OF THE LABORATORY EVALUATIONS

Prior to any field sampling activities, the precision and accuracy of the proposed analytical procedures were determined. The sample preparation and AAS procedures used to analyze field samples for cadmium had an accuracy of 89.2 percent for analyzing known concentrations of cadmium. The precision of these procedures was 1.7 percent.

The precision and accuracy were determined by Parr bomb digestion of four aliquots of a National Bureau of Standards (NBS) "Urban Particulate Matter" #1648, Standard Reference Material (SRM) and three independent analysis techniques: AAS, ICAP spectroscopy, and NAA. The samples were prepared for analysis by Parr bombing the particulate in acid solutions. Four aliquots of the resulting samples were analyzed. Four reagent blanks were also prepared and analyzed using the same procedures. Instrument detection limits for the three techniques were 0.03, 0.03 and 0.12 ug/mL, respectively.

An important part of the accuracy and precision determinations was the precision of the calibration curve. The precision was established by preparing four different sets of standard curves for the AAS and ICAP instruments, and comparing the variability of the curve correlation coefficients. (A correlation coefficient of 0.995 was considered acceptable).

### CALIBRATION CURVE PRECISION

Each calibration curve was constructed by analyzing samples of four different concentrations (0.0, 0.1, 1.0, 2.0 ug/mL) of cadmium in distilled water. These cadmium concentrations were known to be within the linear response range for both AAS and ICAP and were prepared by dilution of a certified standard obtained from Fisher Scientific.

Each standard solution was analyzed in quadruplicate for cadmium by both AAS and ICAP. The absorbance vs. ug/mL was plotted for AAS, and emission units vs. ug/mL was plotted for ICAP. Linear regression analyses were performed to determine the linearity of each curve. A comparison of the four curves indicated that there is excellent agreement between the AAS and ICAP methods for cadmium analysis. The raw analytical data from these curves, and the corresponding linear regression analyses are presented in Appendix B.

The mean AAS correlation coefficient of all four curves was 0.99961, with a standard deviation of 0.00022 and a coefficient of variation (CV) of 0.02 percent. The average ICAP correlation coefficient for the four curves was 0.99991, with a standard deviation of 0.00008 and a CV of 0.008 percent. The ICAP method was shown to be a suitable technique for confirmation of the laboratory evaluation results obtained using AAS.

## ANALYTICAL PRECISION AND ACCURACY COMPARISONS OF AAS, ICAP AND NAA

Precision and accuracy of the analytical procedures were assessed by comparing the cadmium results of the NBS SRM #1648, "Urban Particulate Matter" analyses.

Quadruplicate samples were prepared from the NBS SRM #1648 sample using the following procedures:

1. A 0.5 gram aliquot of an NBS SRM #1648 sample was Parr bombed with one filter paper.
2. The resulting solution was split into two equal samples.
3. One sample was split and analyzed in duplicate by Radian for cadmium using both AAS and ICAP.
4. The other sample was sent to North Carolina State University to be analyzed in duplicate by NAA.
5. Steps 1 through 4 were repeated three times for a total of four sets of samples.

The accuracy (% recovery) and precision (% CV) for all three analytical methods are given in Table 1. Overall average percent recoveries for each analytical method were as follows: 89.2% for AAS, 99.3% for ICAP, and 94.2% for NAA. The mean percent differences for the duplicates was 1.0% for AAS, 6.2% for ICAP, and 1.7% for NAA. In terms

Table 1. ACCURACY AND PRECISION OF CADMIUM IN NBS STANDARD REFERENCE MATERIAL #1648, URBAN PARTICULATE[a]

| Sample ID[b] Number | AAS Accuracy[c] Individual % Recovery | AAS Accuracy[c] Mean | ICAP Accuracy[c] Individual % Recovery | ICAP Accuracy[c] Mean | NAA Accuracy[c] Individual % Recovery | NAA Accuracy[c] Mean |
|---|---|---|---|---|---|---|
| A1 | 97.4 | | 98.3 | | 105.5 | |
| | | 97.4 | | 102.5 | | 106.5 |
| A2 | 97.4 | | 106.6 | | 107.4 | |
| B1 | 84.0 | | 107.5 | | 92.2 | |
| | | 84.7 | | 104.5 | | 91.6 |
| B2 | 85.4 | | 101.5 | | 91.0 | |
| C1 | 81.3 | | 91.3 | | 69.6 | |
| | | 82.0 | | 88.2 | | 70.6 |
| C2 | 82.7 | | 85.0 | | 71.6 | |
| D1 | 92.0 | | 100.1 | | 107.5 | |
| | | 92.7 | | 102.2 | | 108.0 |
| D2 | 93.3 | | 104.2 | | 108.4 | |
| Mean Accuracy | 89.2 | | 99.3 | | 94.2 | |
| % CV (Precision) | 1.7 | | 7.8 | | 17.1 | |
| Duplicate Differences: | | | | | | |
| Mean %:[d] | 1.0 | | 6.2 | | 1.7 | |
| Std. Dev. of Ramdom Error[d,e] | 0.84 | | 4.49 | | 1.09 | |

[a]Based on an NBS cadmium value of 75 ug Cd per gram of particulate.

[b]Sample A was Parr bombed once, Samples B, C, and D were bombed twice.

[c]AAS, Atomic Absorption Spectrophotometry; ICAP, Inductively Coupled Argon Plasma; and NAA Neutron Activation Analysis.

[d]A measure of precision of duplicate determinations on four samples.

[e]Youden, W.J., and E.H. Steiner, "Statistical Manual of the Association of Official Analytical Chemists, "AOAC, Arlington, Virginia 22209 (1975), p. 18.

of standard deviation, the values were 0.84, 4.49, 1.09 ug/g for AAS, ICAP, and NAA, respectively. The duplicate means and the standard deviation are measures of precision for three analytical methods and serve as a basis for assessing the relative precision of the methods.

All three analytical techniques have satisfactory recovery efficiencies to be viable cadmium analysis techniques. One deficiency in the laboratory procedures may be the Parr bombing step (Figure 1 and Figure 2 and Table 1). For AAS, samples B, C, and D which were Parr bombed twice, showed lower recovery than Sample A which was Parr bombed once. However, this trend was not consistently observed for the ICAP and NAA methods of analysis. A single Parr bombing should be used since no clear advantage was apparent and sample manipulation would be minimized.

Many laboratories do not have ICAP instrumentation, and almost none are equipped for NAA. Although both showed higher recovery efficiencies from AAS, neither of these techniques could be recommended for general use as a cadmium measurement method. AAS instrumentation is widely available and relatively easy and inexpensive to use. It provides sufficient sensitivity (i.e., low detection limits), precision and accuracy and is recommended for general use.

## BLANK DETERMINATIONS

Four glass fiber filters were Parr bombed and analyzed in duplicate as blanks. The results are presented in Table 2. The results for AAS, ICAP, and NAA all fell below the instrument detection limits (AAS DL = 0.03 ug/mL; ICAP DL = 0.03 ug/mL; and NAA DL = 0.12 ug/mL. In addition, 5% nitric acid was used to leach sample containers for several days and stainless steel sampling probe nozzles and the teflon-coated filter support were rinsed with nitric acid. Sample train field blanks and reagent blanks were also taken. The cadmium concentrations of all of these solutions were below the detection limits. Therefore, no blank corrections were required for field samples analyzed.

## FIELD SAMPLE ANALYSES

Field sample preparation and analysis was performed as described in Appendix A. Several four point calibration curves (0.0, 0.1, 1.0, and 2.0 ug Cd/ml solution) were constructed before, during, and after

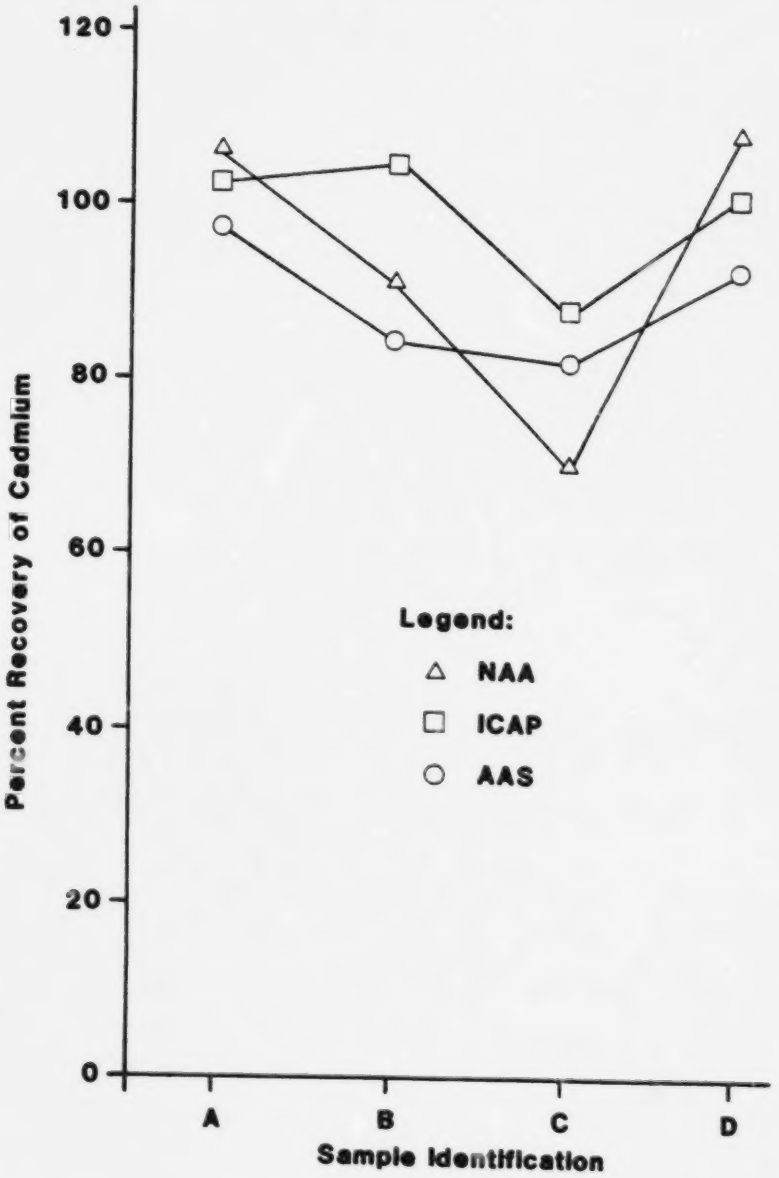


Figure 1. Analysis of NBS urban particulate.

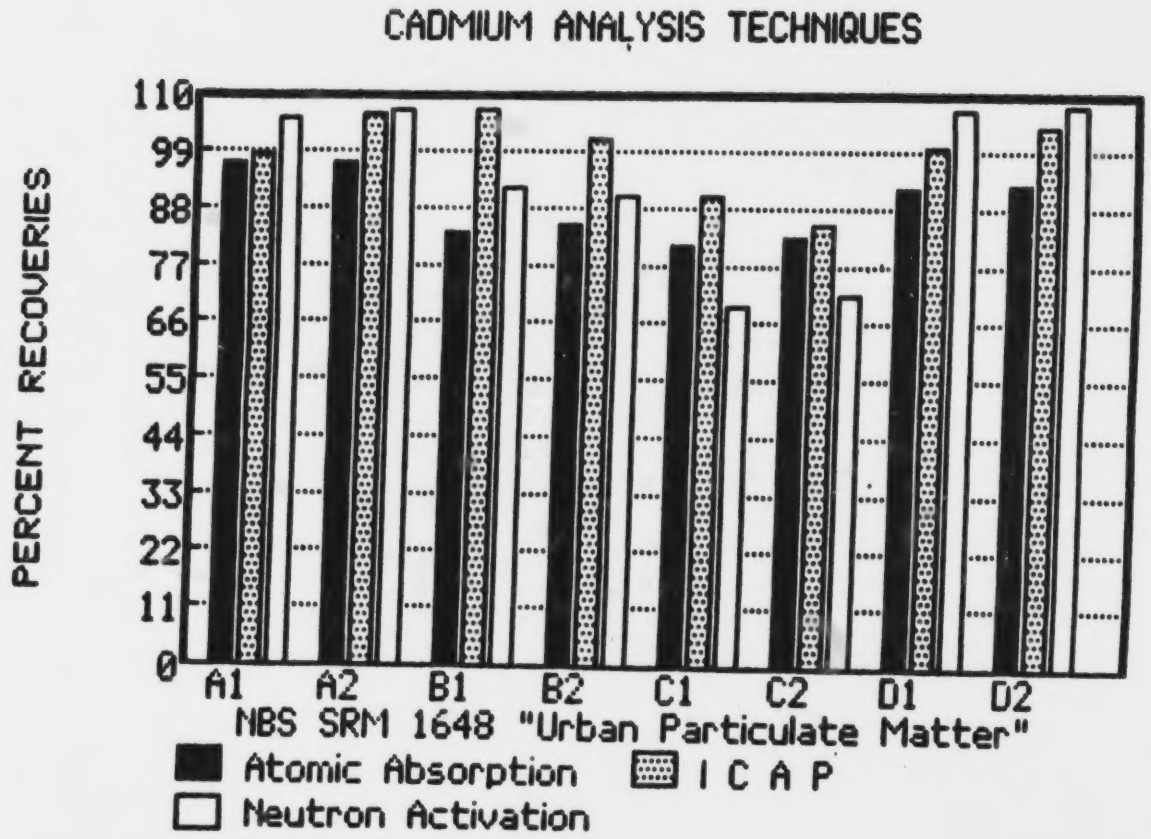


Figure 2. Analysis of urban particulate.

Table 2. FILTER BLANK DETERMINATIONS FOR CADMIUM[a]

| Sample No. | Atomic Absorption | ICAP | Neutron Activation |
|---|---|---|---|
| 10534 | <0.03 | <0.03 | <0.12 |
| duplicate | <0.03 | <0.03 | -- |
| 10535 | <0.03 | <0.03 | <0.12 |
| duplicate | <0.03 | <0.03 | -- |
| 10536 | <0.03 | <0.03 | <0.12 |
| duplicate | <0.03 | <0.03 | -- |
| 10537 | <0.03 | <0.03 | <0.12 |
| duplicate | <0.03 | <0.03 | -- |

[a]All values reported in units of ug/mL.

analysis of the samples. A representative curve is presented in Figure 3. After at least every ten field samples analyzed, a standard near the mid-range of the curve was analyzed to verify instrument stability. Field samples that showed cadmium concentrations greater than 2 ug/ml of Parr-bombed solution were diluted so that the concentration fell within the calibration curve. The results of the analyses of the field samples are shown in Tables 10 and 11 in Section 6.

In addition to the quad-train samples, field train blanks, filter blanks, and reagent blanks were analyzed to determine whether or not any of these components contained background cadmium concentrations. The results of these analyses (as shown in Section 7) indicated that any cadmium contamination was below the instrument detection limit of 0.03 ug Cd/ml.

## RECOMMENDATIONS FOR FUTURE ANALYSES

The range of cadmium concentrations of the samples collected at the field test sites represent a very minor fraction of the cadmium concentration range expected for all stationary sources. Table 3 shows typical stack gas cadmium concentrations for different source categories. As a result of the small linear range of AAS, an important component of analyses of samples from the different source categories is the dilution as shown in Table 3 required to place samples in the AAS linear range.

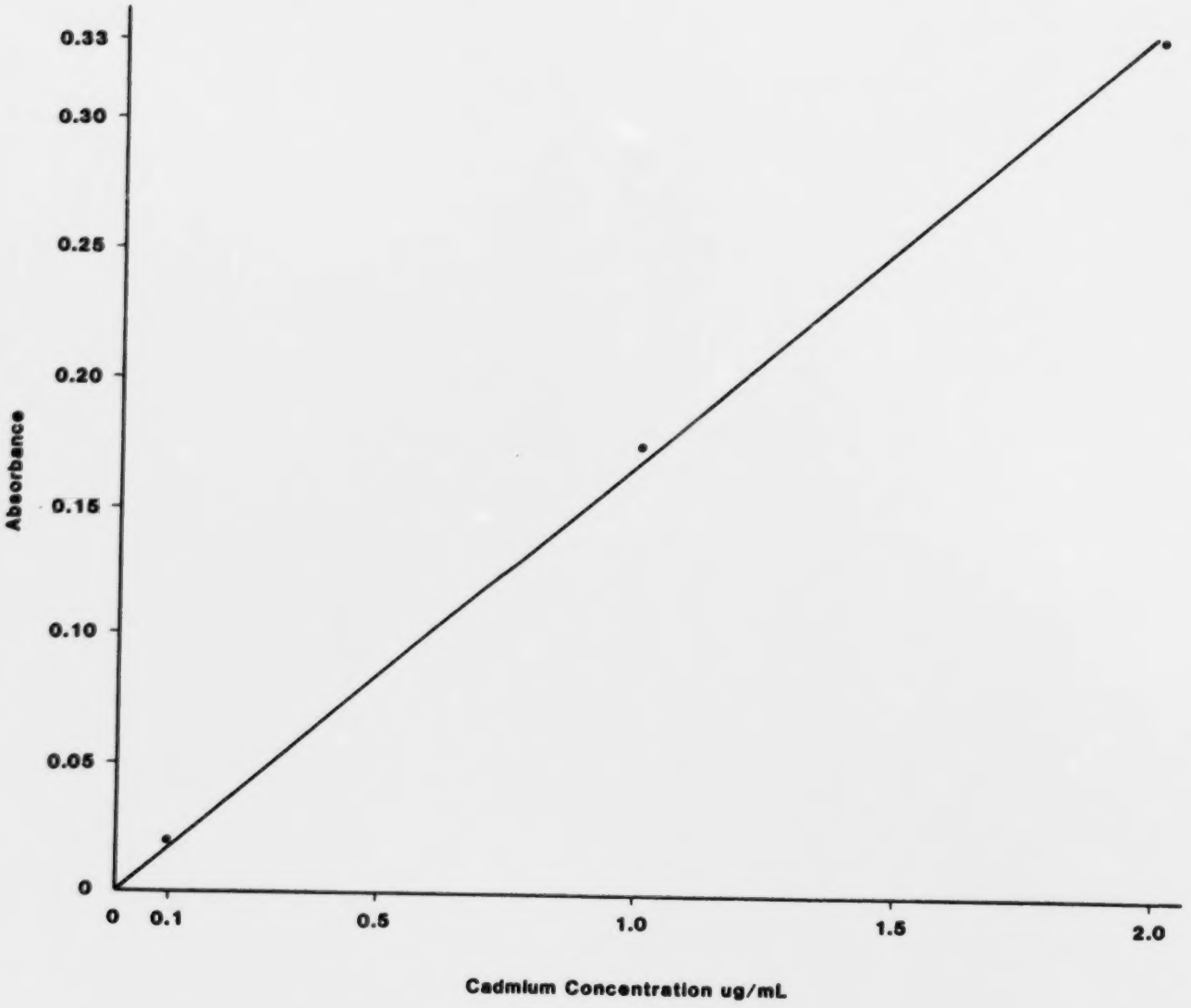


Figure 3. Representative atomic absorption spectrometry calibration curve for cadmium.

Table 3. EXPECTED RANGE OF CADMIUM CONCENTRATIONS FOR VARIOUS CADMIUM SOURCE CATEGORIES

| Source | Expected Cadmium Concentration | AA Dilution[a] | Reference |
|---|---|---|---|
| Municipal Incinerators | 23-230 ug/$m^3$ | up to 4X dilution | Test data from host site |
| Primary Cadmium Smelters | 9-7424 ug/$m^3$ (cadmium oxide baghouse) | up to 125X dilution | Human Exposure Model inputs for cadmium source assessment document |
| Sewage Sludge Incinerators | 20-30 ug/$m^3$ | none required | |
| Coal Combustion (uncontrolled) | 49-230 ug/$m^3$ | up to 4X dilution | Conventional Combustion Environmental Assessment and F Factors from EPA Method 19 |
| Oil Combustion (uncontrolled) | 29-80 ug/$m^3$ | dilute 2X | |
| Primary Zinc Smelters | 864-7424 ug/$m^3$ | dilute 14-125X | Human Exposure Model inputs for cadmium source assessment document |
| Zinc Oxide | 36-8464 ug/$m^3$ | up to 141X dilution | |
| Primary lead Smelter | 11-875 ug/$m^3$ | up to 14X dilution | |

[a]Need for dilution based upon an upper range of 2 ug/ml linearity for AA. Sample volume 0.85-1.7 dscm and 50 ml total volume after digestion.

## SECTION 6

## RESULTS OF THE FIELD EVALUATION

The field testing portion of this study was designed to evaluate each of the following:

- The cadmium collection efficiency of the front and back halves of the modified EPA Method 5 (MM5) train,
- The precision of the sampling and sample recovery procedures, and
- The effect of the sample volume on the ability of the method to detect cadmium.

The first field test was conducted at a municipal waste incinerator which had previously been tested for cadmium emissions. Cadmium concentrations reported during the previous testing ranged from 23 to 230 ug/dscm. The range of cadmium found during this study ranged from 32 to 115 ug/dscm. The second field test was performed at a municipal sewage sludge multiple hearth incinerator. The range of cadmium concentration reported for this study was 836 to 1,137 ug/dscm. Except for one run during the first field test, the sampling method employed for both tests was a MM5 train which used nitric acid in the first two impingers instead of water. Separate analyses were performed on the front and back halves of the trains to determine the collection efficiency of each half.

In order to assess sampling and sample recovery precision, four "identical" samples were collected simultaneously using a quad-probe. Four simultaneous samples were collected for a total of 24 and 16 samples for tests one and two, respectively. Sampling was conducted isokinetically for all test runs.

Sample volumes collected during the field tests were nominally 30 and 60 dscf (0.9 to 1.8 dscm). The corresponding method detection limit for these sample volumes is 0.050 and 0.025 ug Cd/dscf (1.7 and 0.84 ug Cd/dscm). Based on the previous cadmium emissions testing, cadmium detection was not expected to be a problem; however, the total volume was varied to determine the resulting effect on the cadmium analysis.

## PROCESS DESCRIPTION

### Field Test #1

The test site selected for the first field test was a mass burn municipal solid waste incineration plant. The plant disposes of up to 2250 tons per day of municipal refuse, while generating steam used in a turbine generator to produce electricity for sale.

The facility consists of three parallel process lines designated as Units 1, 2, and 3. Each line is designed to burn up to 750 tons per day of refuse. The refuse moves through the furnace on Von Roll reciprocating grates. Combustion temperatures typically reach 2500$^{o}$F (1370$^{o}$C)in the incinerator. The gases from the combustion zone contact water walls, a generator, and superheater tube banks to produce steam.

### Field Test #2

The test site selected for the second field test was a municipal sewage sludge multiple hearth incineration plant. The incinerator is rated at 7 tons per hour.

The solids removed from various treatment units at the plant are pumped to a sludge receiving tank which also receives sludge pumped from another plant. These solids (sludge) are pumped to a thickening tank and then dewatered on filter presses to a solid sludge cake. The sludge cake is conveyed to an incinerator where it is burned at a very high temperature (1400$^{o}$F), reducing the solids to an inert ash. The ash is then disposed of in a landfill. The high temperature within the incinerator destroys any bacteria and oderous gases from the sludge. The plant process diagram is shown in Figure 4. The plant production data for the two field test periods are shown in Tables 4 and 5.

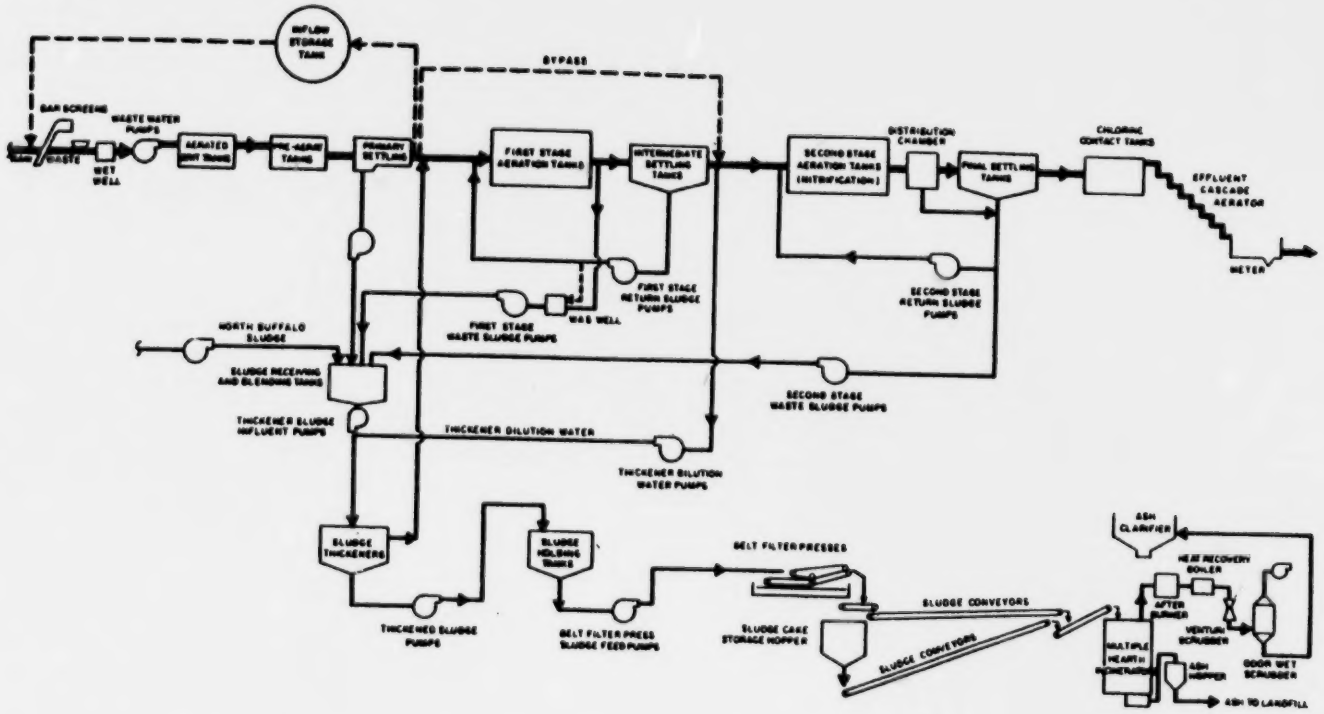


Figure 4. Treatment plant schematic flow diagram.

Table 4. PLANT PRODUCTION DATA FOR FIELD TEST #1

| Date | Time | Test No. | Steam Rate (lbs/hr x 1000) |
|---|---|---|---|
| 10/29/85 | 0900 | | 189 |
| | 1001 | 1 | 193 |
| | 1030 | 1 | 185.8 |
| | 1045 | 1 | 184.2 |
| | 1101 | 1 | 175.4 |
| | 1115 | 1 | 190.6 |
| | 1130 | 1 | 182.9 |
| | 1145 | 1 | 196.8 |
| | 1201 | 1 | 184.0 |
| | 1215 | 1 | 180.6 |
| | 1230 | | 193.4 |
| | 1245 | | 182.2 |
| | 1301 | | 182.9 |
| | 1315 | | 193.1 |
| | 1330 | | 191.7 |
| | 1345 | | 176.6 |
| | 1401 | | 188.0 |
| | 1415 | | 198.8 |
| | 1430 | | 181.5 |
| | 1445 | | 198.1 |
| | 1501 | | 200.6 |
| | 1515 | | 171.1 |
| | 1530 | | 187.1 |
| | 1545 | | 190.1 |
| | 1600 | 2 | 181 |
| | 1640 | 2 | 177.9 |
| | 1700 | 2 | 190 |
| | 1800 | 2 | 187 |
| Steam Rate Average 0900-1800 | | | =186.4 |
| Test #1 Average | | | =185.9 |
| Test #2 Average | | | =184 |
| 10/30/85 | 0750 | | 189.9 |
| | 0801 | | 187.2 |
| | 0815 | | 189.6 |
| | 0830 | | 189.6 |
| | 0845 | | 194.2 |
| | 0901 | | 195.0 |
| | 0915 | | 188.4 |
| | 0930 | | 204.9 |
| | 0945 | | 192.9 |
| | 1001 | | 199.8 |
| | 1015 | | 183.1 |
| | 1030 | | 181.1 |
| | 1045 | | 188.8 |
| | 1101 | | 180.1 |
| | 1115 | | 189.7 |
| | 1130 | | 186.4 |
| | 1145 | | 188.6 |
| | 1201 | | 197.1 |
| | 1215 | 3 | 189.3 |
| | 1230 | 3 | 183.6 |
| | 1245 | 3 | 186.2 |
| | 1301 | 3 | 188.9 |
| | 1315 | 3 | 183.6 |
| | 1330 | 3 | 186.8 |
| | 1345 | 3 | 194.1 |
| | 1401 | | 188.4 |
| | 1415 | | 192.6 |
| | 1430 | | 186.8 |
| | 1445 | | 178.9 |
| | 1501 | | 188.7 |
| | 1515 | | 190.2 |
| | 1530 | | 185.5 |
| | 1545 | | 188.1 |
| | 1601 | | 180.4 |
| | 1615 | | 190.9 |
| | 1630 | | 184.9 |
| | 1645 | | 185.6 |
| 10/30/85 | 1701 | 4 | 182.2 |
| | 1715 | 4 | 191.5 |
| | 1730 | 4 | 189.8 |
| | 1745 | 4 | 195.3 |
| | 1801 | 4 | 191.8 |
| | 1815 | 4 | 181.6 |
| | 1830 | 4 | 185.1 |
| | 1845 | 4 | 188.2 |
| | 1901 | 4 | 182.4 |
| | 1915 | 4 | 185.6 |
| | 1930 | 4 | 198.2 |
| | 1945 | 4 | 190.4 |
| | 2001 | 4 | 179.8 |
| | 2015 | 4 | 193.6 |
| | 2030 | 4 | 185.7 |
| | 2045 | 4 | 191.7 |
| | 2101 | | 199.8 |
| | 2115 | | 190.4 |
| Steam Rate Average 0750-2115 | | | =188.8 |
| Test #3 Average | | | =187.5 |
| Test #4 Average | | | =188.3 |
| 10/31/85 | 0915 | | 182.6 |
| | 0930 | | 193.0 |
| | 0945 | | 172.0 |
| | 1001 | | 213.5 |
| | 1015 | | 202.1 |
| | 1030 | | 188.0 |
| | 1045 | | 182.2 |
| | 1101 | 5 | 181.5 |
| | 1115 | 5 | 182.1 |
| | 1130 | 5 | 184.3 |
| | 1145 | 5 | 196.2 |
| | 1201 | 5 | 195.9 |
| | 1215 | 5 | 194.9 |
| | 1230 | 5 | 178.4 |
| | 1245 | 5 | 191.8 |
| | 1301 | 5 | 180.4 |
| | 1315 | 5 | 192.8 |
| | 1330 | | 185.2 |
| | 1345 | | 175.6 |
| | 1401 | | 190.1 |
| | 1415 | | 187.9 |
| | 1430 | | 176.6 |
| | 1445 | | 207.0 |
| | 1501 | | 187.6 |
| | 1515 | | 186.3 |
| | 1530 | | 163.2 |
| | 1545 | 6 | 193.8 |
| | 1601 | 6 | 183.9 |
| | 1615 | 6 | 183.1 |
| | 1630 | 6 | 192.4 |
| | 1645 | 6 | 137.7 |
| | 1701 | 6 | 97.7 |
| Steam Rate Average 0915-1701 | | | =183.1 |
| Test #5 Average | | | =187.8 |
| Test #6 Average | | | =164.8 |
| Steam Rate Average for the 3 days of Recorded Data | | | =186.7 |

Table 5. PLANT PRODUCTION DATA FOR FIELD TEST #2

| Date | Time | Feed Rate (TPH) | Radian Test No. |
|---|---|---|---|
| 7-23-86 | 1300 | 3.0 | |
| | 1400 | 4.7 | |
| | 1500 | 4.7 | |
| | 1600 | 4.7 | 1 |
| | 1700 | 4.5 | 1 |
| | 1800 | 4.5 | 1 |
| | 1900 | 4.3 | |
| | 2000 | 3.8 | |
| 7-25-86 | 1300 | 0.0 | |
| | 1400 | 0.0 | |
| | 1500 | 0.4 | 2 |
| | 1600 | 2.6 | 2 |
| | 1700 | 4.3 | 2 |
| | 1800 | 4.5 | 2 |
| | 1900 | 4.8 | |
| | 2000 | 3.6 | |
| | 2100 | 4.3 | 3 |
| | 2200 | 5.1 | 3 |
| | 2300 | 3.6 | 3 |
| | 2400 | 5.1 | |
| 7-26-86 | 1000 | 4.6 | |
| | 1100 | 4.7 | |
| | 1200 | 4.9 | 4 |
| | 1300 | ~4.4[a] | 4 |
| | 1400 | ~4.4[a] | 4 |
| | 1500 | ---[a] | |

[a]Not recorded on log sheet for three hours. The plant shut down at 1408. The last totalizer reading was taken at 1600. The 4.4 TPH is estimated based on the totalizer readings taken at 1200 and 1600.

## SAMPLING LOCATIONS AND APPARATUS

### Sampling Locations

#### Field Test #1

The flue gases were sampled at the No. 1 ESP outlet breeching prior to the induced draft fan. A side view of the test location is shown in Figure 5, while a top view, including the quad train, is shown in Figure 6. The breeching is rectangular, with interior dimensions of 124 inches by 76 inches. The equivalent diameter of the duct is 94.2 inches for the purpose of selecting the required number of sampling points by EPA Method 1[7]. The test ports are located approximately 30 feet (3.8 equivalent duct diameters) downstream of a 90 degree bend, and approximately 10 feet (1.3 diameters) upstream of the ID fan inlet.

Six sampling ports were available at the sampling location. EPA Method 1 requires a 24 point traverse for this location so a 6 x 4 test grid was used and a velocity traverse was performed prior to testing. The results of this velocity traverse are shown in Figure 7. As Figure 7 shows, point D-2 has an average velocity very close to the duct average velocity and is located at a normal EPA Method 5 matrix point away from the stack wall. This point served as the sampling nozzle location for this study.

#### Field Test #2

The flue gases were sampled at the scrubber exhaust stack downstream of the induced draft fan. The stack has a 31 inch internal diameter. The ports were located 12 feet downstream of the I.D. fan and 15 feet upstream of a silencer. A velocity traverse was performed to verify the quad probe placement. The results of this velocity traverse are shown in Figure 8. The stack was checked and found to have non-cyclonic flow.

As Figure 8 shows, the center of stack has an average velocity very close to the duct average velocity. This center point served as the sampling position for this study (representative of stack emission levels).

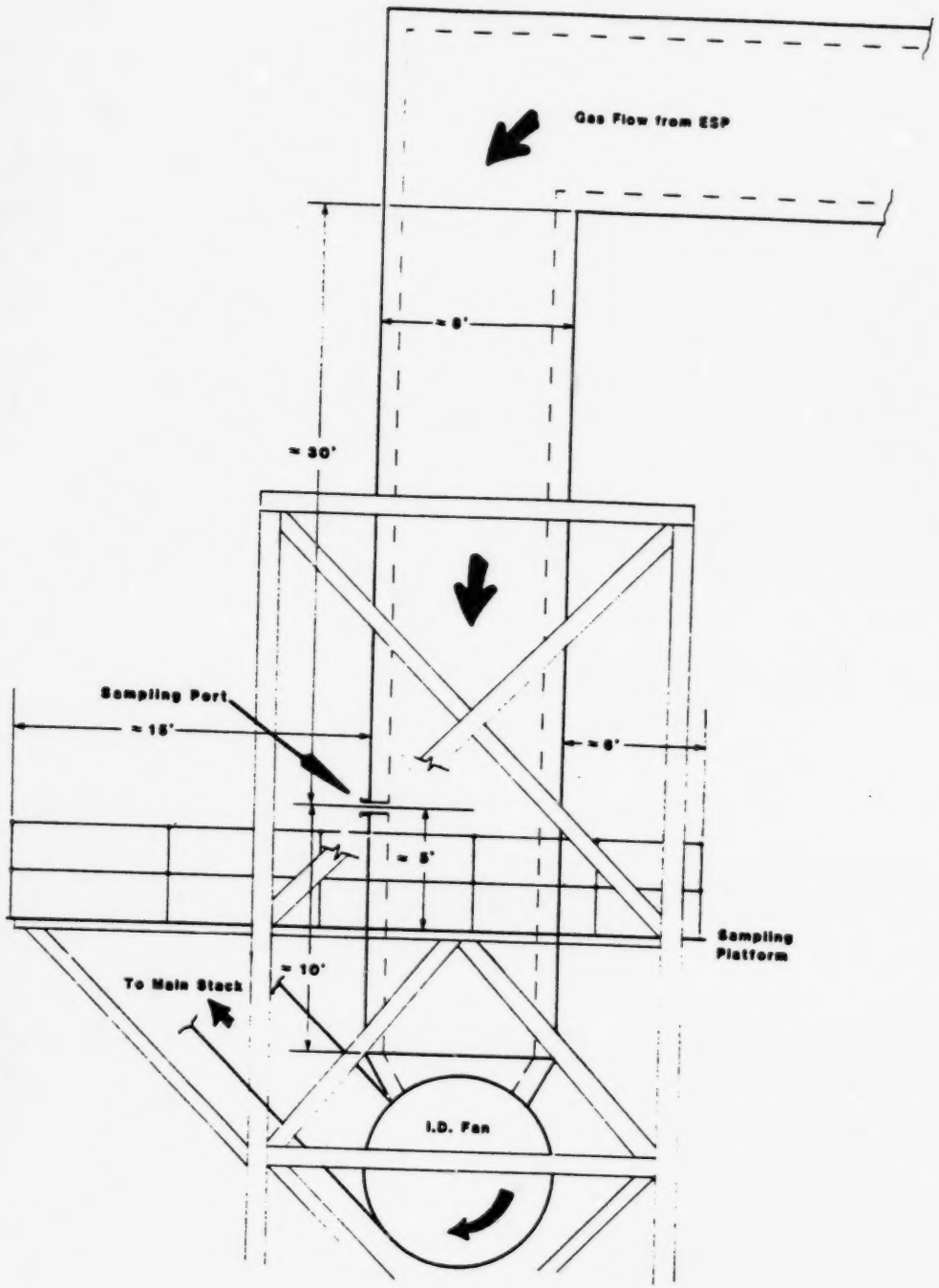


Figure 5. Sampling location - side view.

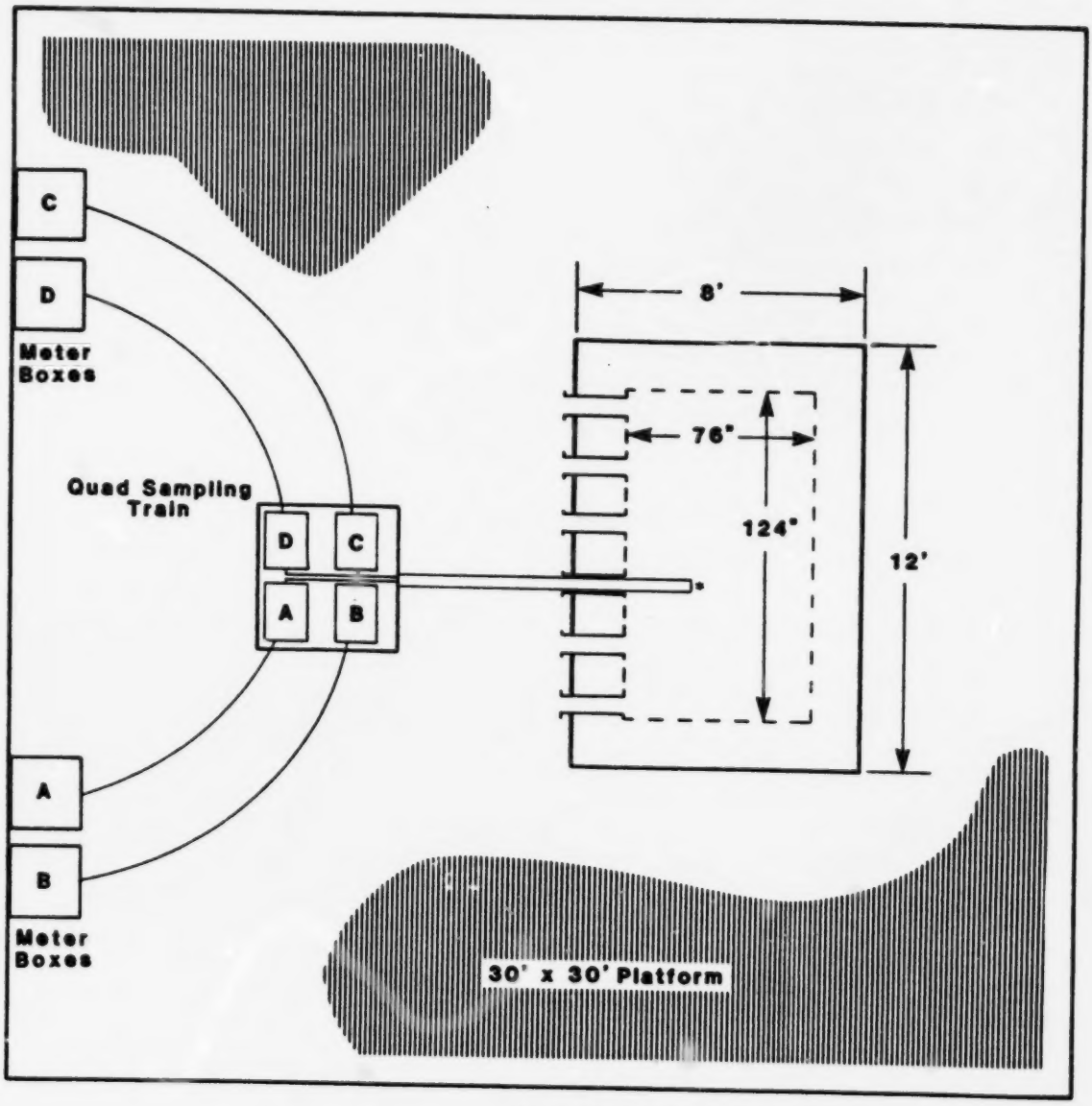


Figure 6. Sampling location - top view (including the quad train).

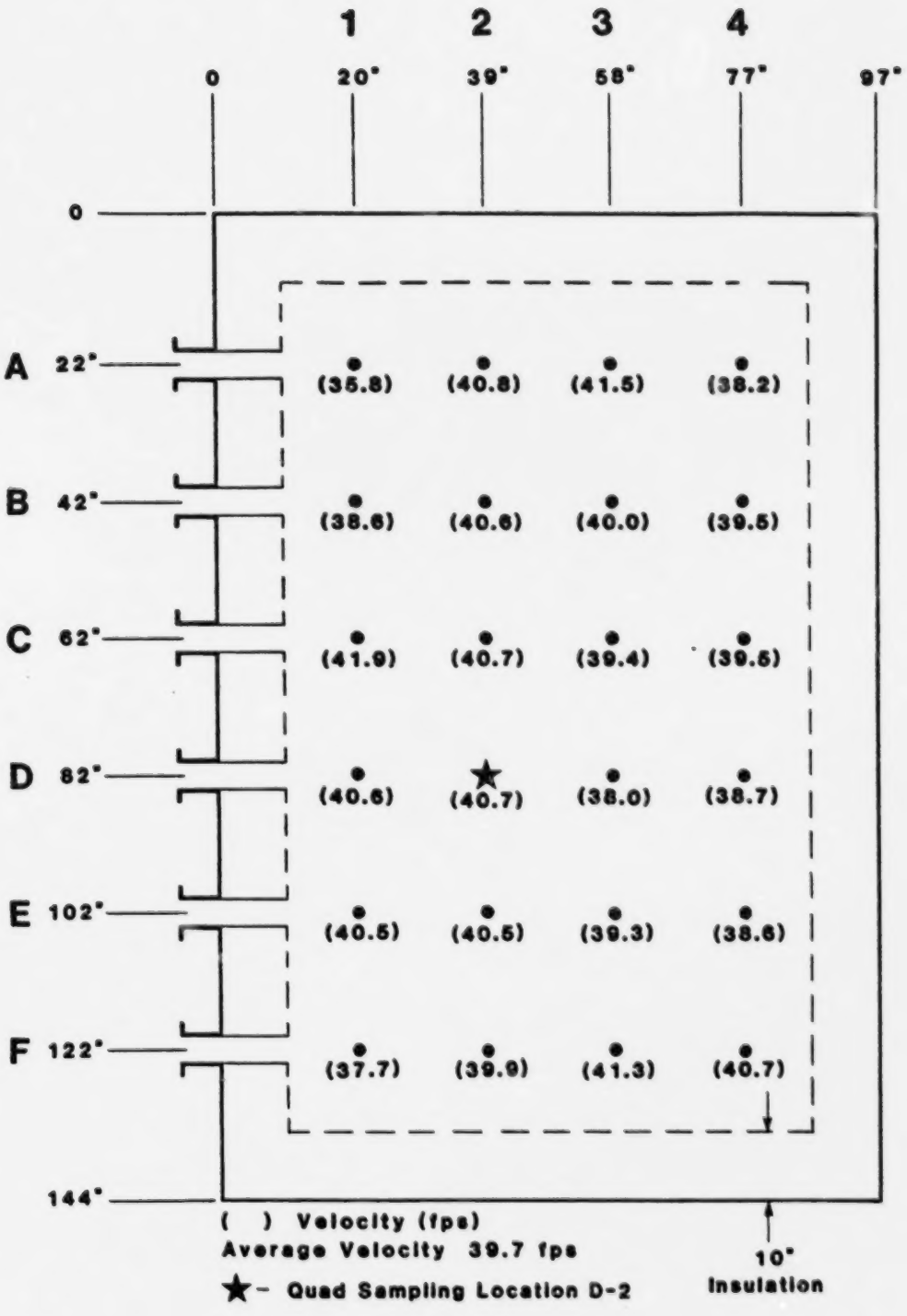


Figure 7. Sampling location - velocity profile.

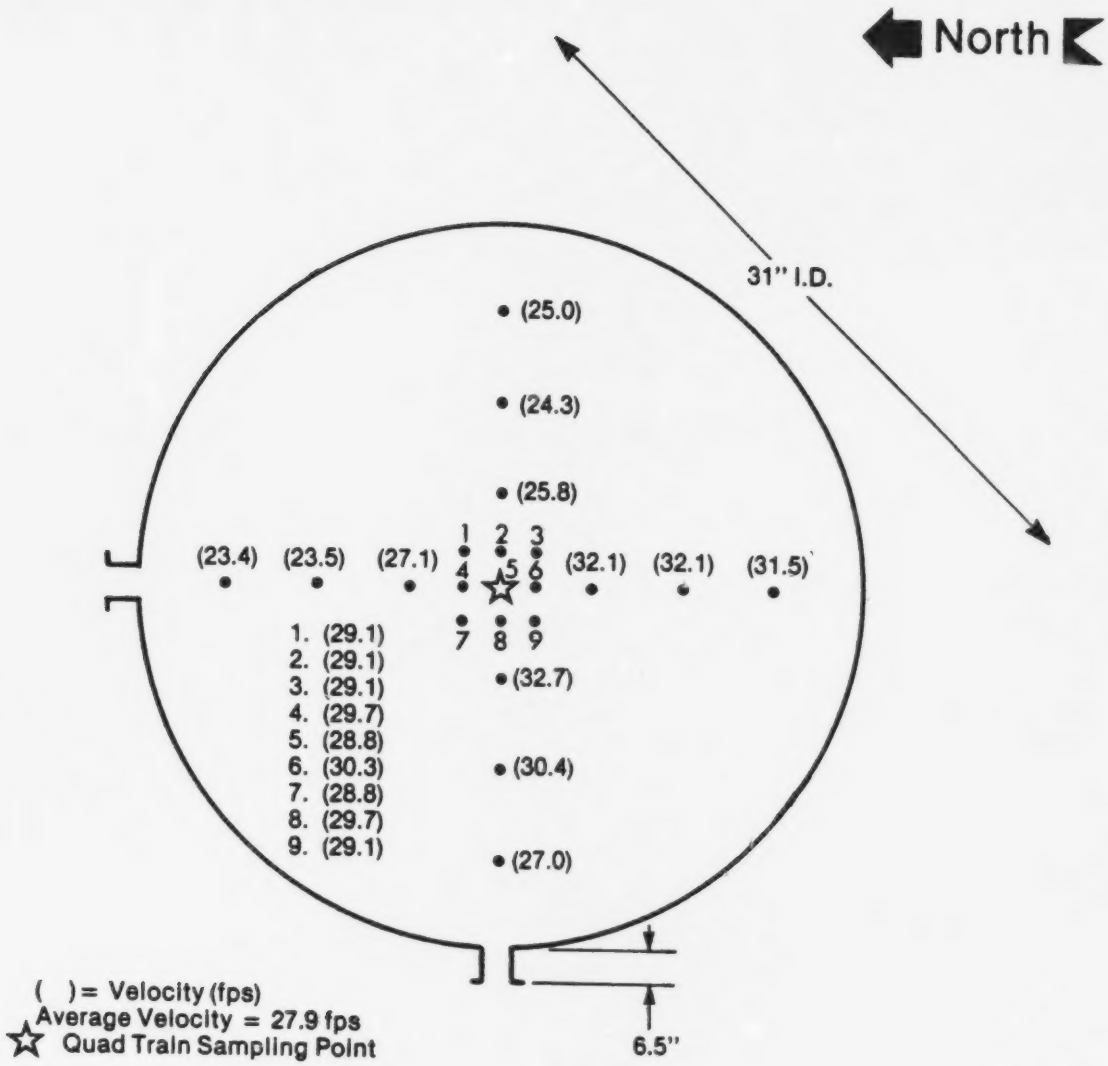


Figure 8. Sampling Location - Velocity Profile

Sampling Apparatus

The overall quad train design used in both field tests is shown in Figure 9. Details of the arrangement of the nozzles are shown in Figure 10. The size and complexity of the quad train prevents traversing of the duct. Therefore, sampling was conducted at a single point during each test series.

Figure 11 shows a MM5 cadmium sampling train. Each of the four trains in the quad set-up was run as an individual cadmium train. A heated 90 degree glass elbow was used to connect each glass filter housing to its respective glass probe liner in each train.

## EXPERIMENTAL DESIGN AND SAMPLE COLLECTION

The test configurations for the field tests are shown in Tables 6 and 7. Actual sample volumes and sampling times were reasonably close to the targeted values specified by EPA. Small differences occurred because the samples were being taken isokinetically. The field test sampling data is presented in Appendix D.

Six quad-train sampling runs were conducted over a three-day period for the first field test. The sampling rate used was approximately 0.5 dscfm. Three one-hour runs and three two-hour runs were conducted in order to determine what effect total sample volume had on precision and the ability to detect cadmium.

The second field test consisted of four quad-train sampling runs conducted over a three-day period. The sampling rate was again approximately 0.5 dscfm. One one-hour run and three two-hour runs were conducted.

The field samples were collected according to the procedures outlined in Appendix A, "Sampling and Analysis Procedures for the Determination of Cadmium from Combustion Sources." Single-point sampling was performed isokinetically with four colocated trains, as shown in Figures 6 and 8. Deviations from the prescribed sampling procedures are documented in Section 7, Quality Assurance/Quality Control Activities.

## TRAIN AND REAGENT BLANKS

Prior to the first field test, an entire cleaned sampling train was recovered, and containers were filled with nitric acid and allowed to sit for several days as described in Section 5 in order to establish

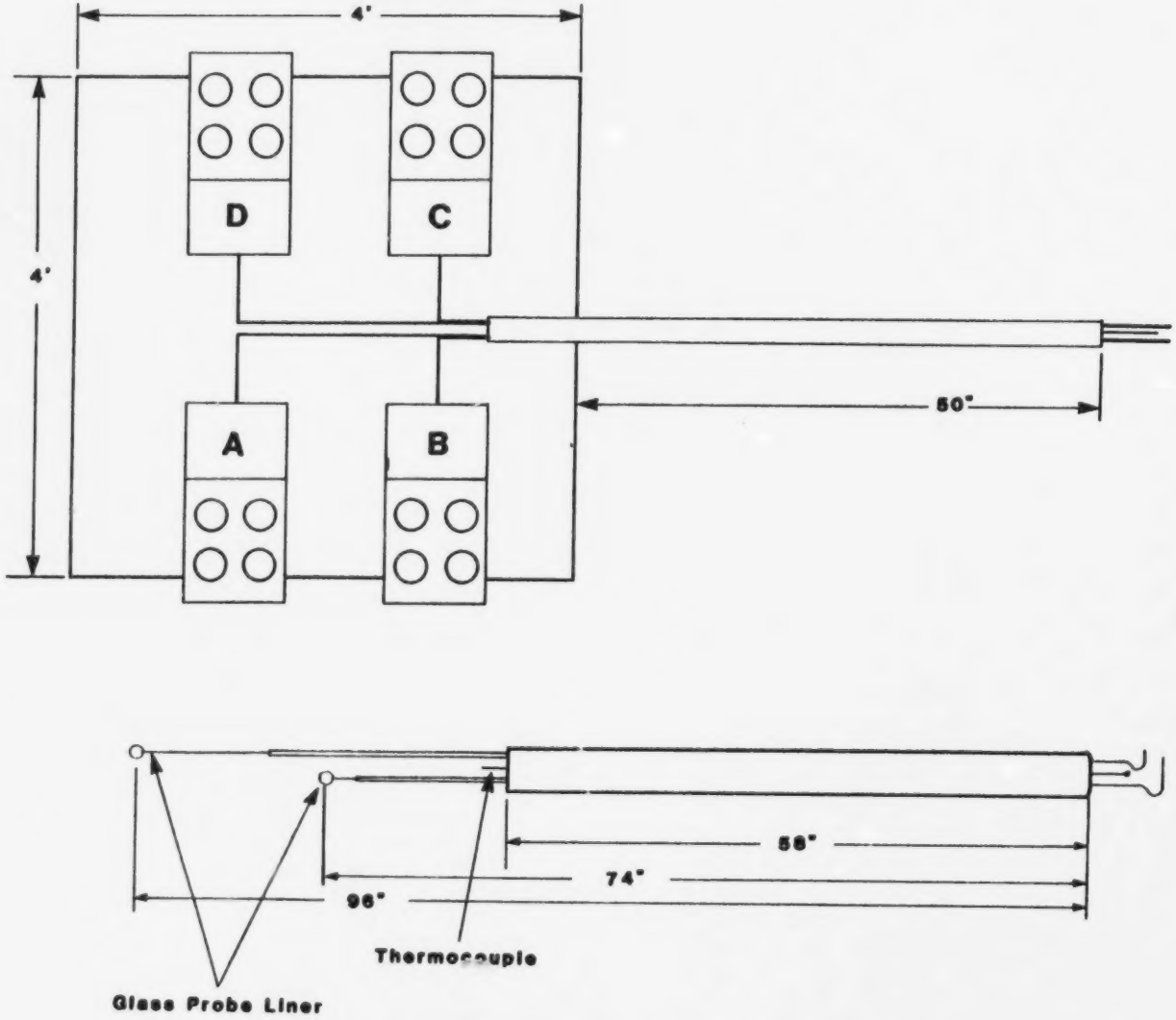


Figure 9. Quad train configuration method as used during cadmium validation test.

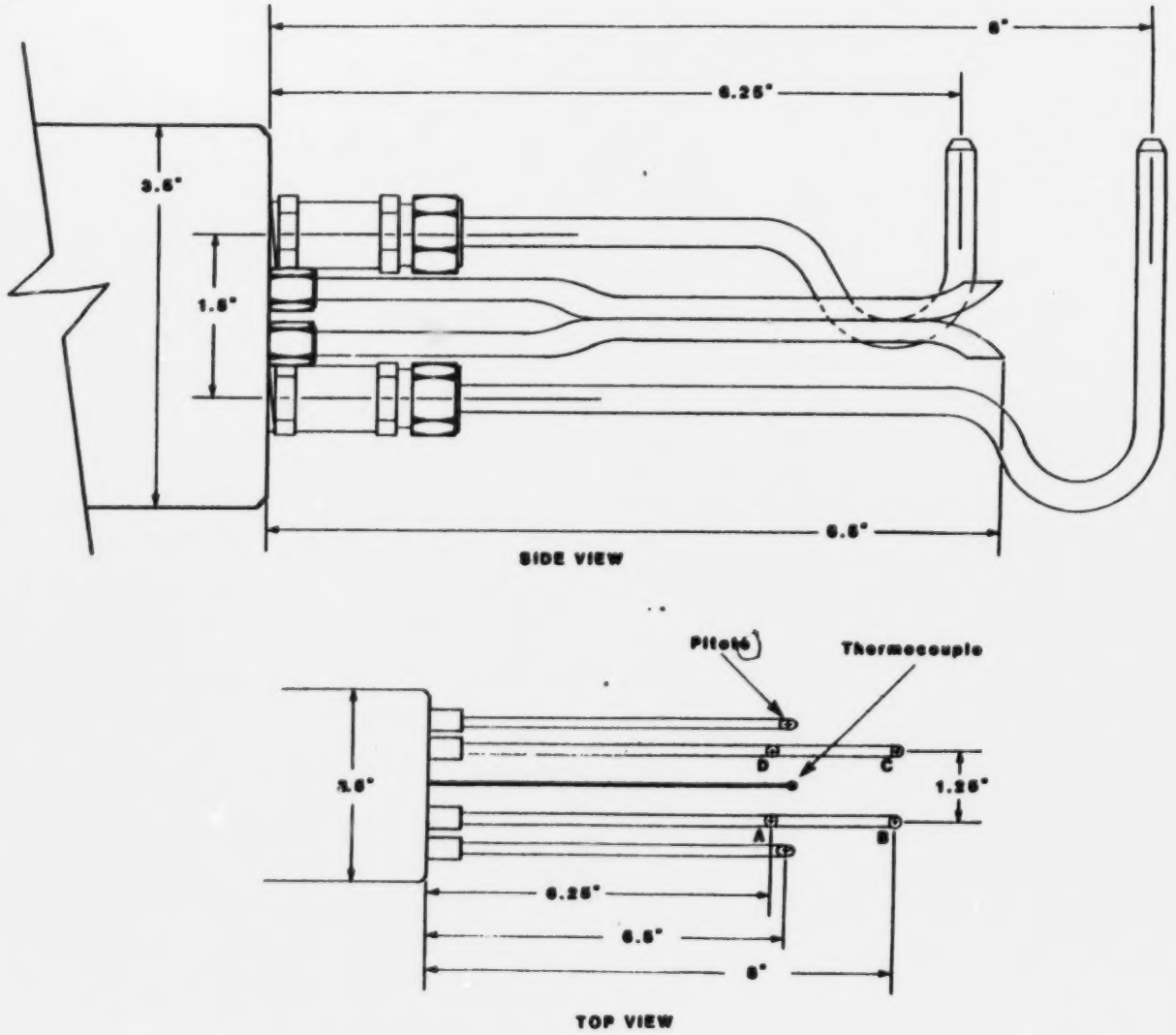


Figure 10. Quad probe sampling nozzle configuration.

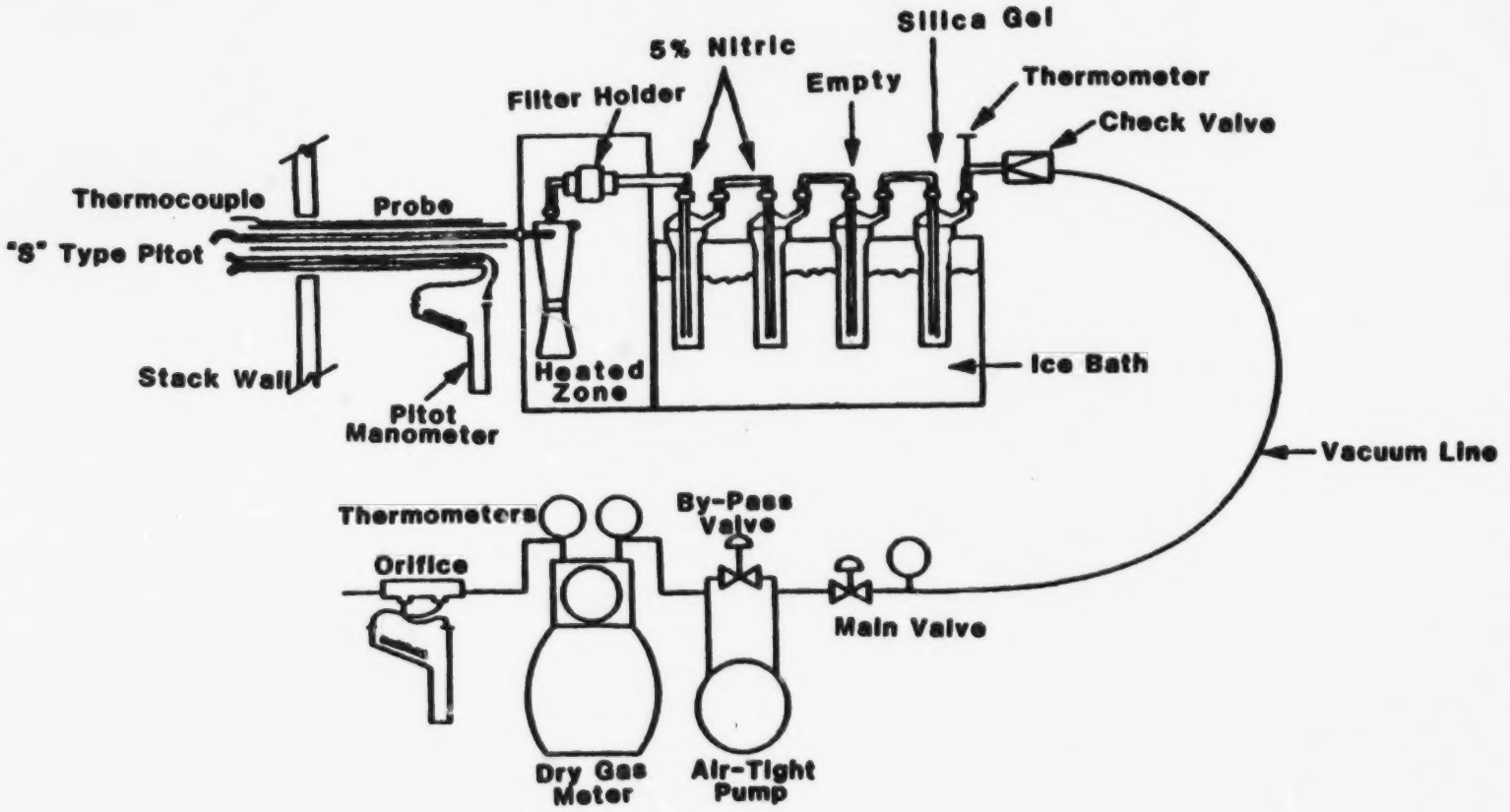


Figure 11. MM5 cadmium sampling train.

Table 6. TEST CONFIGURATION FOR THE FIRST CADMIUM SAMPLING FIELD TEST*

| | | AM Train | | | | PM Train | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | A | B | C | D |
| Day 1 | Target Time, mins | 120 | 120 | 120 | 120 | 60 | 60 | 60 | 60 |
| | Actual time, mins | 130 | 130 | 130 | 130 | 65 | 65 | 65 | 65 |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | 30 | 30 | 30 | 30 |
| | Actual sample volume, DSCF | 65 | 65 | 65 | 65 | 32.5 | 32.5 | 32.5 | 32.5 |
| Day 2 | Target time, mins | 60 | 60 | 60 | 60 | 120 | 120 | 120 | 120 |
| | Actual time, mins | 70 | 70 | 70 | 70 | 130 | 130 | 130 | 130 |
| | Desired sample volume, DSCF | 30 | 30 | 30 | 30 | 60 | 60 | 60 | 60 |
| | Actual sample volume, DSCF | 35 | 35 | 35 | 35 | 65 | 65 | 65 | 65 |
| Day 3 | Target time, mins | 120 | 120 | 120 | 130 | 60 | 60 | 60 | 60 |
| | Actual time, mins | 130 | 130 | 130 | 130 | 70 | 70 | 70 | 70 |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | 30 | 30 | 30 | 30 |
| | Actual sample volume, DSCF | 65 | 65 | 65 | 65 | 35 | 35 | 35 | 35 |

*Isokinetic flowrates were maintained at nominally, 0.5 DSCFM.

Table 7. TEST CONFIGURATION FOR THE SECOND CADMIUM SAMPLING FIELD TEST*

| | | 2-Hour Train | | | | 1-Hour Train | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | A | B | C | D |
| Day 1 | Target Time, mins | 120 | 120 | 120 | 120 | | | | |
| | Actual time, mins | 120 | 120 | 120 | 120 | | | | |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | | | | |
| | Actual sample volume, DSCF | 59.1 | 59.2 | 63.3 | 62.1 | | | | |
| Day 2 | Target time, mins | 120 | 120 | 120 | 120 | 60 | 60 | 60 | 60 |
| | Actual time, mins | 120 | 120 | 120 | 120 | 60 | 60 | 60 | 60 |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | 30 | 30 | 30 | 30 |
| | Actual sample volume, DSCF | 74.2 | 73.5 | 78.8 | 76.3 | 30.2 | 30.2 | 32.3 | 31.4 |
| Day 3 | Target time, mins | 120 | 120 | 120 | 120 | | | | |
| | Actual time, mins | 118.5 | 118.5 | 118.5 | 118.5 | | | | |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | | | | |
| | Actual sample volume, DSCF | 60.4 | 60.0 | 64.3 | 63.3 | | | | |

*Isokinetic flowrates were maintained at nominally, 0.5 DSCFM.

sit for several days as described in Section 5 in order to establish that cadmium would not leach from sampling train components or sample containers. Analysis of these solutions were performed prior to arriving on-site and showed less than 0.03 ug/mL Cd (i.e., samples were below detection limits).

While on site during both field tests, a used sampling train was recharged and recovered. Cadmium was not detected, indicating that the recovery and cleanup procedures were satisfactory (i.e., they had not left any Cd in the train) at either site. Blanks were taken of all the reagents, filters, and solvents used at both sites. Cadmium levels were below 0.03 ug/ml for all of these blanks.

## ANALYTICAL RESULTS AND DISCUSSION

One of the variables evaluated in this study was the precision of the sampling and sample recovery procedures. Tables 8 and 9 present the cadmium concentrations and precision assessments for the quad-train field studies. The between train pooled standard deviations were 12.39 ug/dscm (field test #1) and 38.0 (field test #2) and represent the overall precision for the field studies. In terms of percent coefficient of variation, the pooled precision was 13.54 and 3.79, which is a measure of the precision of sampling and analysis for tests 1 and 2, respectively.

The within-run or between-train precision shown in the tables is assessed in terms of a standard deviation and percent coefficient of variation. Contributions to these variables result from (1) differences in the sampling trains, (2) variations between trains in the sample preparation and recovery steps, and (3) analytical variability. Between-test pooled variability includes all of the above in addition to: (1) the day-to-day variability of the cadmium concentration in the feed, (2) effects of different plant operating conditions and (3) the potential effect of within-run variability on the cadmium collection. Proper consideration should be given to the apparent lack of homogeneity among the percent coefficient of variations prior to using further these precision estimates for calculating confidence intervals or for testing for comparisons of means.

Table 8. CADMIUM CONCENTRATIONS AND WITHIN-RUN PRECISION ASSESSMENTS FOR FIELD TEST #1

| Test No. | Sample Train A | B | C | D | Average x | Standard[a] Deviation | Percent Coefficient of Variation, % CV |
|---|---|---|---|---|---|---|---|
| 1 | 32.2 | 32.8 | 30.4 | 32.6 | 32.0 | 1.10 | 3.4 |
| 2 | 96.5 | 85.6 | 87.2 | 104.1 | 93.4 | 8.63 | 9.2 |
| 3 | 105.5 | 115.5 | 73.5 | 74.9 | 92.4 | 21.36 | 23.1 |
| 4 | 76.2 | 88.0 | 101.2 | 76.7 | 84.8 | 11.67 | 13.8 |
| 5 | 80.0 | 111.5 | 103.3 | 88.3 | 95.8 | 14.24 | 14.9 |
| 6 | 101.4 | 328.0[b] | 93.8 | 95.6 | 96.93 | 3.97 | 4.1 |
| | | | | | pooled | 12.39[d] | 13.54[d] |

[a]All sample train results reported in micrograms cadmium per dry standard cubic meter, ug/dscm.

$$\left[\frac{\text{probe rinse + filter + impingers (ug)}}{\text{total volume of stack gas sampled } (m^3)}\right]$$

[b]This value was excluded from the data analysis, because when subjected to a Dixon Outlier test[c] for Test No. 6, it did not meet the acceptance criterion of 126.1 ug/dscm, at the 5 percent level of significance (i.e., 95% probability).

[c]The Dixon outlier test may be found in Dixon, Wilford J., and Frank J. Massey, Jr., "Introduction to Statistical Analysis," McGraw-Hill Book Company, New York (1957).

[d]$$\text{pooled} = \left(\sum_{i=1}^{n} \frac{s_i^2}{n}\right)^{1/2}$$

Table 9. CADMIUM CONCENTRATIONS AND WITHIN-RUN PRECISION ASSESSMENTS FOR FIELD TEST #2

| Test No. | Sample Train A | B | C | D | Average x | Standard[a] Deviation | Percent Coefficient of Variation, % CV |
|---|---|---|---|---|---|---|---|
| 1 | 886.2 | 927.8 | 835.5 | 886.6 | 884.0 | 37.8 | 4.27 |
| 2 | 1,137.1 | 1,133.4 | 1,081.9 | 1,081.4 | 1,108.5 | 31.0 | 2.80 |
| 3 | 989.1 | 1,088.0 | 993.6 | 1,057.5 | 1,032.1 | 48.7 | 4.71 |
| 4 | 1,097.8 | 1,041.1[c] | 1,030.9 | 1,081.9 | 1,062.9 | 32.0 | 3.01 |
| | | | | | pooled | 38.0[b] | 3.79[b] |

[a]All sample train results reported in micrograms cadmium per dry standard cubic meter, ug/dscm.

$$\left[\frac{\text{probe rinse + filter + impingers (ug)}}{\text{total volume of stack gas sampled } (m^3)}\right]$$

[b]$$\text{pooled} = \left(\sum_{i=1}^{n} \frac{s_i^2}{n}\right)^{1/2}$$

[c]The filter in this run was faulty and it leaked some cadmium to the impingers. However, only 3 percent of the total cadmium catch for this train was in the impingers, and 97 percent was in the front half.

A second variable which was addressed was the collection efficiency of the sampling train. Except for Run 4-B in Test #2, no cadmium was detected in the back half, indicating that the filter was very efficient in preventing breakthrough. Cadmium (about 55 ug) was found in the first two impingers of the back half of Run 4-B of the second field test because gas bypassed a faulty filter. Particulate could be seen in the glass connections between the filter holder and the first impinger.

Field Test #1

A third variable evaluated in the data set of Table 8 is the length of the sampling period for each run. Tests 2, 3, and 6 were each conducted for roughly one hour while Runs 1, 4, and 5 were conducted for about 2 hours. An analysis of variance confirmed that there was not a significant difference in the variabilities of the cadmium concentrations of the one-hour compared to the two-hour runs, at the 5% level of significance (95% probability). Thus, sampling times of about one hour will yield concentration data equivalent to that for double the sampling time.

There were several anomalies in the cadmium concentration data set for the first field test. The average cadmium concentration level in Test No. 1 was much lower than for Tests 2 through 6. The cadmium concentrations reported for Tests 2 through 6 in Table 8 reflect a reasonably constant average cadmium concentration in the stack gas. However, there is no reason to suspect that the Test No. 1 samples were collected any differently than other test run samples. Therefore, these data were included in the data analysis. The concentration difference between Run No. 1 and the other runs is expected to be due to plant feed materials or operating conditions.

Also, Sample B in test number 6 shows an extremely high value in terms of cadmium per dscm (Table 8). Table 10 shows a comparison of cadmium in terms of gas volume sampled and the amount of cadmium per gram of particulate. Sample B, test number 6, is suspected to have been contaminated either by a large amount of cadmium after the sample was collected, or by a few particles extremely rich in cadmium which may have been pulled into this particular train. The Dixon outlier test indicates that this value is an outlier (i.e., it should not be considered in the statistical analysis).

Table 10. COMPARISON OF FIELD TEST #1 CADMIUM CONCENTRATIONS, PARTICULATE CONCENTRATION, CADMIUM TO PARTICULATE CONCENTRATION, AND ISOKINETIC RATES FOR EACH RUN[a]

| | Train | | | |
|---|---|---|---|---|
| Test No. | A | B | C | D |
| 1 | | | | |
| Cadmium (mg/dscm) | 0.0322 | 0.0328 | 0.0304 | 0.0326 |
| Particulate (mg/dscm) | b | b | b | b |
| Cadmium to Particulate (mg/gram) | b | b | b | b |
| Isokinetic Value (%) | 102.2 | 104.1 | 102.6 | 107.6 |
| 2 | | | | |
| Cadmium (mg/dscm) | 0.0965 | 0.0856 | 0.0872 | 0.1041 |
| Particulate (mg/dscm) | b | b | b | b |
| Cadmium to Particulate (mg/gram) | b | b | b | b |
| Isokinetic Value (%) | 100.8 | 104.2 | 99.9 | 100.4 |
| 3 | | | | |
| Cadmium (mg/dscm) | 0.1055 | 0.1155 | 0.0735 | 0.0749 |
| Particulate (mg/dscm) | 38.77 | 38.78 | 49.48 | 36.05 |
| Cadmium to Particulate (mg/gram) | 2.72 | 2.98 | 1.48 | 2.08 |
| Isokinetic Value (%) | 102.8 | 100.0 | 103.5 | 101.0 |
| 4 | | | | |
| Cadmium (mg/dscm) | 0.0762 | 0.0850 | 0.1012 | 0.0767 |
| Particulate (mg/dscm) | 224.12[c] | 34.25 | 33.77 | 32.59 |
| Cadmium to Particulate (mg/gram) | c | 2.48 | 3.00 | 2.35 |
| Isokinetic Value (%) | 101.4 | 101.2 | 103.1 | 102.9 |
| 5 | | | | |
| Cadmium (mg/dscm) | 0.0800 | 0.1115 | 0.1033 | 0.0883 |
| Particulate (mg/dscm) | 40.73 | 44.21 | 37.19 | 34.54 |
| Cadmium to Particulate (mg/gram) | 1.96 | 2.52 | 2.78 | 2.56 |
| Isokinetic Value (%) | 102.6 | 101.1 | 102.2 | 101.5 |
| 6 | | | | |
| Cadmium (mg/dscm) | 0.1014 | 0.3280[d] | 0.0938 | 0.0956 |
| Partculate (mg/dscm) | 37.87 | 38.93 | 35.37 | 32.42 |
| Cadmium to Particulate (mg/gram) | 2.68 | 8.42[d] | 2.65 | 2.95 |
| Isokinetic Value (%) | 101.0 | 100.0 | 97.7 | 101.2 |

[a]The particulate emission and cadmium-to-particulate ratio values presented in this table are for information only. In any municipal waste incineration process, significant variation might be expected of particulate or cadmium emissions between tests.

[b]Particulate weight was not determined.

[c]Not valid for particulate concentration or cadmium-to-particulate ratio because of broken probe liner which resulted in excessive particulate weight values.

[d]Not valid for cadmium, Dixon outler test.

Table 10 shows a particulate value for Sample A in test number 4 which is nearly seven times higher than other values of the data set. For this particular sample, the glass probe liner broke during, or just prior, to sampling. A large amount of milky material was noted in the two nitric acid impingers, and the filter appeared brownish rather than white. Even though the particulate value for this sample was very high, the concentration of cadmium appeared to agree with the other three runs of the test and was therefore included in the statistical analysis. Finally, the comparison of the cadmium collection efficiency of impingers containing nitric acid versus impingers containing distilled water was inconclusive. Cadmium was not detected in the train back half for any run of Field Test #1.

Field Test #2

In Field Test #2, there were no apparent outliers in the cadmium concentrations, either on the basis of mg/dscm, or mg Cd/g particulate, as seen in Table 11. Average run concentrations in mg/dscm ranged from 0.8866 mg/dscm to 1.1085 mg/dscm. An analysis of variance indicated that there was a significant difference between runs, which was not unexpected. Within-run precision, measured in percent coefficient of variation, (% CV) ranged from 2.80 to 4.71, indicating consistent and precise sampling and analysis capability under the test conditions encountered in the second field test. It is to be noted that the average cadmium concentration in Field Test #1 ranged from 32.0 ug/dscm to 96.93 ug/dscm for 6 runs, while in the second field test, cadmium concentrations ranged from 886.6 to 1,108.5 ug/dscm for 4 runs. As noted above, the precision in Field Test #2 was consistent, exhibiting a narrow range of variability between runs. Table 8 shows the precision, or between run variability, for Field Test #1 to range from 3.4 to 23.1 in terms of percent CV. Runs 1 and 6 of Field Test #1 show percent CV of 3.4 and 4.1, respectively, which is in the same range of precision as the four runs of Field Test #2. These results suggest that the overall method precision (sampling and analysis) is probably not a function of the average concentration (e.g. in ug/dscm) over the concentration range from about 30 to 1100 ug/dscm. Such factors as source variability over

Table 11. COMPARISON OF FIELD TEST #2 CADMIUM CONCENTRATIONS, PARTICULATE CONCENTRATION, CADMIUM TO PARTICULATE CONCENTRATION, AND ISOKINETIC RATES FOR EACH RUN[a]

| Test No. | A | B | C | D |
|---|---|---|---|---|
| 1 | | | | |
| Cadmium (mg/dscm) | 0.8862 | 0.9278 | 0.8355 | 0.8866 |
| Particulate (mg/dscm) | 120.98 | 121.27 | 120.81 | 120.88 |
| Cadmium to Particulate (mg/gram) | 7.33 | 7.60 | 6.91 | 7.04 |
| Isokinetic Value (%) | 93.7 | 92.5 | 100.4 | 97.0 |
| 2 | | | | |
| Cadmium (mg/dscm) | 1.1371 | 1.1334 | 1.0819 | 1.0814 |
| Particulate (mg/dscm) | 189.91 | 194.87 | 193.16 | 204.38 |
| Cadmium to Particulate (mg/gram) | 5.99 | 5.85 | 5.60 | 5.29 |
| Isokinetic Value (%) | 99.3 | 96.7 | 105.5 | 100.6 |
| 3 | | | | |
| Cadmium (mg/dscm) | 0.9891 | 1.0880 | 0.9936 | 1.0575 |
| Particulate (mg/dscm) | 170.60 | 175.74 | 181.88 | 173.23 |
| Cadmium to Particulate (mg/gram) | 5.79 | 6.19 | 5.46 | 6.11 |
| Isokinetic Value (%) | 97.8 | 96.5 | 104.6 | 100.0 |
| 4 | | | | |
| Cadmium (mg/dscm) | 1.0978 | 1.0411[b] | 1.0309 | 1.0817 |
| Particulate (mg/dscm) | 205.96 | 208.82 | 203.08 | 206.61 |
| Cadmium to Particulate (mg/gram) | 5.33 | 5.11 | 5.07 | 5.24 |
| Isokinetic Value (%) | 97.4 | 95.1 | 105.4 | 100.3 |

[a]The particulate emission and cadmium-to-particulate ratio values presented in this table are for information only.

[b]The filter in this run was faulty and it leaked some cadmium to the impingers. However, only 3 percent of the total cadmium catch for this train was in the impingers, and 97 percent was in the front half.

the sampling period and quality control by the sampling and analysis personnel are probably more important than the average cadmium concentration level in determining the overall precision.

During Field Test #2, one NBS SRM urban particulate sample was analyzed for cadmium. The results showed a 5% bias (or 95% recovery) which is indicative of the accuracy of the analytical results for Field Test #2. A second in-house audit sample was prepared from a secondary cadmium standard and showed a bias of -16.6% or 83.4% recovery.

The method of addition was used to assess matrix effects for Train B of each sample run. Reanalysis of all four samples after spiking showed results within 10% of the expected values, indicating no adverse matrix effects.

For Field Test #1, the impinger solutions were adjusted to a known volume and analyzed directly. For Field Test #2, the impinger solutions were adjusted to a known volume and one aliquot was boiled to near dryness. The digested sample was then reconstituted to one-half the original volume and analyzed. The impinger solutions were also analyzed directly. In one train of one run, because of a faulty filter, cadmium reached the impingers in the amount of three percent of the total cadmium catch for that train. The analysis of the digested sample of the impingers from this train indicated that it contained about 50 ug of cadmium, while the analysis of the undigested sample indicated about 60 ug.

A greenish residue was noted in most of the impingers of Field Test 2 after the nitric acid solutions had been transferred. As a check for possible cadmium which may not have been recovered from the impinger, the four impingers from run #2 were rinsed a final time with acetone which removed the greenish residue from the impingers. The acetone was evaporated to dryness and the residue digested with 5% nitric acid. These solutions were analyzed and found to contain no measurable cadmium.

# SECTION 7

# QUALITY ASSURANCE AND QUALITY CONTROL

This section discusses the Quality Assurance and Quality Control (QA/QC) procedures implemented for the field test evaluation of the cadmium Modified EPA Method 5 quad-train sampling technique. The objectives of the QA program and a summary of the QC activities are discussed.

## QA PROGRAM OBJECTIVES

The cadmium method evaluation incorporated a comprehensive QA/QC plan which emphasized (1) adherence to prescribed sampling procedures, (2) careful documentation of sample collection and field data, (3) the use of chain-of-custody records, (4) adherence to prescribed analytical procedures, and (5) implementation of independent systems audits. The overall objective of this plan was to produce complete, representative, and comparable data of known quality.

## SUMMARY OF QA/QC ACTIVITIES

This section provides a summary of QA/QC activities and results for three main areas: field sampling, laboratory analysis, and audits. Additional detail on the activities associated with the sampling and analytical efforts is provided in the Quality Assurance Project Plans (QAPP) for the individual field tests.

### Sampling Activities

Quality control for the flue gas sampling centered around (1) equipment calibration, (2) glassware and sampling equipment cleaning, (3) procedural QC checks, and (4) sample custody procedures. Key activities and QC results for each of these areas are discussed below.

Pretest calibrations or inspections were conducted on pitot tubes, sampling nozzles, temperature sensors, and analytical balances. Both pre and post-test calibrations were also performed on the dry gas meters used for the quad-train sampling. All of this equipment met the calibration criteria specified in the QA Plans. Differences between pre- and post-test dry gas meter calibrations for each of the runs were less than 2.0 percent.

An extensive pre-cleaning procedure was implemented for all sample train glassware, sample containers, and sampling tools. This cleaning procedure, which is outlined in Table 12, was implemented to minimize the potential for contamination with substances that may have interfered with the analysis for cadmium. All sample train glassware was capped prior to use and stored in a dust-free environment. A clean sample trailer was maintained for train assembly and sample recovery. To document the effectiveness of the glassware pre-cleaning procedure, a sample train "proof blank" was obtained at both tests. The proof blank was obtained from a complete set of Method 5 sample train glassware that had been cleaned by the procedure in Table 12. The pre-cleaned glassware was rinsed with the sample recovery solvents and the rinses were analyzed for cadmium. Results of the proof blank analyses for both field tests, which are presented in Tables 13 and 14, showed no problems with interferences.

Procedural QC activities during manual gas sampling for cadmium focused on:

- visual equipment inspections,
- utilization of sample train blanks,
- ensuring the proper sampling location,
- conducting pre-test and post-test sample train leak checks,
- maintaining proper temperatures at the filter housing, sorbent trap, and impinger train,
- maintaining isokinetic sampling rates, and
- recording all data on preformatted field data sheets.

Table 12. CADMIUM GLASSWARE PRECLEANING PROCEDURES

Field Test #1

1. Soak all glassware in hot soapy water (Alconox$^{R}$).
2. Rinse with distilled/deionized $H_2O$.
3. Rinse with a 5 percent nitric acid solution.
4. Rinse 3 times with distilled/deionized $H_2O$.
5. Rinse with acetone and allow to air dry in a contamination-free environment.

Field Test #2

1. Soak all glassware in hot soapy water (Alconox$^{R}$).
2. Rinse with tap water.
3. Fire glassware at 450$^{o}$C for 4 hours.
4. Soak for at least 8 hours in 10% nitric acid.
5. Rinse 3 times with distilled/deionized $H_2O$.
6. Rinse with acetone and allow to air dry in a contamination-free environment.

Table 13. FIELD TEST #1 ANALYTICAL RESULTS FOR CADMIUM MODIFIED EPA METHOD 5 FIELD BLANKS USING AAS

| Sample Number* | Description | Amount of Cadmium Detected (ug/ml)[a] |
|---|---|---|
| 10726/58 | First day train blank, 10/29/85 | <0.03 |
| 10730/63 | Train blank, sample trailer, 10/28/85 | <0.03 |
| 10735 | Second day train blank, 10/30/85 | <0.03 |
| 10752 | Acetone reagent blank | <0.03 |
| 10805 | $HNO_3$ blank | <0.03 |
| 10806 | DI $H_2O$ blank | <0.03 |
| 10807 | 5% $HNO_3$ impinger and rinse blank | <0.03 |
| 10808 | Second day 5% $HNO_3$ impinger and rinse blank | <0.03 |
| 10809 | First day 5% $HNO_3$ impinger and rinse blank | <0.03 |

*Each sample was analyzed in duplicate and the mean value was reported. The AAS detection limit was 0.03 ug/mL.

Table 14. FIELD TEST #2 ANALYTICAL RESULTS FOR CADMIUM MODIFIED EPA METHOD 5 FIELD BLANKS USING AAS

| Description | Amount of Cadmium Detected (ug/ml)[a] |
|---|---|
| Proof Blank | <0.03 |
| Field Blank | <0.03 |
| Probe Blank (Nitric Acid Rinse) | <0.03 |
| Filter Blank | <0.03 |
| Filter Blank Plus Front Half Filter Rinse | <0.03 |
| Back Half Acetone Rinse | <0.03 |
| $HNO_3$ Blank | <0.03 |
| Acetone Blank | <0.03 |

[b]Each sample was analyzed in duplicate and the mean value was reported. The AAS detection limit was 0.03 ug/mL.

Results of isokinetic calculations and leak checks for the quad-train cadmium sampling are presented in Tables 15 and 16. The QA objectives for each test run were a leak free ($\leq$0.02 cfm) sample train and an average isokinetic sampling rate of 100$\pm$10 percent.

As shown in the tables, the isokinetics objective was met for all test runs. Initial and final leak checks for the sampling train were performed for each test run. No leaks were detected for any of the test runs. A probe was found to be broken at the end of test run 4-A during field test #1. The actual time that the breakage occurred during sampling is not known. The train A sample taken during this test run was found to be valid for the determination of cadmium.

Sample custody procedures used during this program emphasized careful documentation of the samples collected and the use of chain-of-custody records for samples transported to the laboratory for analysis. Steps taken to identify and document samples collected included labeling each sample with a unique alphanumeric code and logging the sample in a master logbook. Each sample container lid was individually sealed with teflon tape and a chain-of-custody sticker to ensure that samples were not tampered with.

Analytical Activities

Laboratory analyses were conducted during the cadmium studies to determine the cadmium and particulate concentrations of flue gas samples.

Quality control activities for these analyses are described in detail in the individual site specific QA Plans. Instruments were calibrated daily with certified standards to establish calibration and to verify proper instrument operation.

Cadmium samples were prepared and analyzed by Radian's RTP laboratory. The primary analytical measurement technique was Flame Atomic Absorption Spectrophotometry (AAS) for cadmium. After the solid residues were weighed, the residue was combined with the filter for subsequent Parr bombing. Associated QC activities included the use of sample blanks, control samples, solvent blanks, and duplicate analyses (see Table 17).

Table 15. SUMMARY OF FIELD TEST #1 ISOKINETIC CALCULATIONS AND LEAK CHECK RESULTS FOR THE MODIFIED EPA METHOD 5 CADMIUM SAMPLING

| Test Run | Outlet Isokinetics | Meets QC Objective | Leak Check[a] |
|---|---|---|---|
| 1-A | 102.2 | Yes | Good |
| 1-B | 104.1 | Yes | Good |
| 1-C | 102.6 | Yes | Good |
| 1-D | 107.6 | Yes | Good |
| 2-A | 100.8 | Yes | Good |
| 2-B | 104.2 | Yes | Good |
| 2-C | 99.9 | Yes | Good |
| 2-D | 100.3 | Yes | Good |
| 3-A | 102.8 | Yes | Good |
| 3-B | 99.9 | Yes | Good |
| 3-C | 103.5 | Yes | Good |
| 3-D | 101.0 | Yes | Good |
| 4-A | 101.4 | Yes | Good |
| 4-B | 101.2 | Yes | Good |
| 4-C | 103.1 | Yes | Good |
| 4-D | 102.9 | Yes | Good |
| 5-A | 102.6 | Yes | Good |
| 5-B | 101.1 | Yes | Good |
| 5-C | 102.2 | Yes | Good |
| 5-D | 101.5 | Yes | Good |
| 6-A | 101.0 | Yes | Good |
| 6-B | 99.9 | Yes | Good |
| 6-C | 97.7 | Yes | Good |
| 6-D | 101.2 | Yes | Good |

[a]A "good" leak check is defined as a sample train leak less than 0.02 CFM at the maximum vacuum encountered during the test.

Table 16. SUMMARY OF FIELD TEST #2 IOSKINETIC CALCULATIONS AND LEAK CHECK RESULTS FOR THE MODIFIED EPA METHOD 5 CADMIUM SAMPLING

| Test Run | Outlet Isokinetics | Meets QC Objective | Leak Check[a] |
|---|---|---|---|
| 1-A | 93.7 | Yes | Good |
| 1-B | 92.5 | Yes | Good |
| 1-C | 100.4 | Yes | Good |
| 1-D | 97.1 | Yes | Good |
| 2-A | 99.3 | Yes | Good |
| 2-B | 96.7 | Yes | Good |
| 2-C | 105.5 | Yes | Good |
| 2-D | 100.6 | Yes | Good |
| 3-A | 97.8 | Yes | Good |
| 3-B | 96.5 | Yes | Good |
| 3-C | 104.6 | Yes | Good |
| 3-D | 100.0 | Yes | Good |
| 4-A | 97.4 | Yes | Good |
| 4-B | 95.1 | Yes | Good |
| 4-C | 103.4 | Yes | Good |
| 4-D | 100.3 | Yes | Good |

[a]A "good" leak check is defined as a sample train leak less than 0.02 CFM at the maximum vacuum encountered during the test.

Table 17. SUMMARY OF CADMIUM ANALYTICAL QUALITY CONTROL CHECKS

| Quality Control Check | Frequency of Analysis | Acceptance Criteria[a] | Met Acceptance Criteria | |
|---|---|---|---|---|
| | | | Field Test #1 | Field Test #2 |
| Field Blanks | One used flue gas sampling train after recovery | Free of contamination at the minimum detectable limit | Yes | Yes |
| | One flue gas sampling train (before use, after lab cleaning | | Yes | Yes |
| Solvent Blank | One per washing solution | Free of contamination at the minimum detectable limit | Yes | Yes |
| Calibration Check Sample | 2 calibration standards analyzed daily, prior to analyses | ±10% of theoretical value | Yes | Yes |
| Mid-level Calibration Standard | At the end of analyses each day | ±10% of theoretical value | Yes | Yes |
| Filter Blank | Clean filter papers for each batch to be used in the sample train, analyzed in duplicate | Blank filter; cadmium concentration must be subtracted from each field sample concentration | Blank value was less than minimum detectable limit | Blank value was less than minimum detectable limit |
| Duplicate Samples | Every sample analyzed in duplicate | Percent difference within ±10 | Yes | Yes |
| In-Process Calibration | All 4 calibration solutions analyzed in duplicate after each 10 samples are analyzed | The mean of the duplicate analyses of each calibration standard must fall within the 99% confidence interval | Yes | Yes |

[a]Minimum detectable limit of 0.03 ug/ml of cadmium.

## Audit Activities

The audit activity for the cadmium program consisted of an independent systems audit of the first field testing effort by the on-site QC monitor. The objectives of the systems audit were to: (1) evaluate adherence to the QA Plan, (2) document test procedures used, (3) provide information to allow assessment of data quality, and (4) make recommendations that could improve data quality. The field systems audit report is presented as Appendix C.

The systems audit showed that all field activities were being performed with strict adherence to the QA Plan. The only modification from the QA Plan protocol was the replacement of the 5% nitric acid with water in the A and B trains of test run 5. This change was implemented at the request of the EPA Project Officer, Thomas E. Ward. The results of the corresponding distilled water blank were presented in Table 13.

## REFERENCES


1. Quality Assurance Handbook for Air Pollution Measurements Systems, Volume III - Stationary Source Specific Methods. EPA-600/4-77-027b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977.

2. Lentzen, D. E., et al. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Second Edition. Prepared for Industrial Environmental Research Laboratory, Office of Energy, Minerals and Industry, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

3. Cawse, P. A. Intercomparison of Analysis of Air Filter Deposits for Trace Elements. United Kingdom Atomic Energy Research Establishment Report, AERE-R 8191, 1976.

4. Ranweiler, L. E. and Moyers, J. L. Atomic Absorption Procedure for Analysis of Metals in Atmospheric Particulate Matter, Environ. Sci. and Tech. 8(2):153, 1974.

5. Ranweiler, L. E. and Moyers, J. L. Atomic Absorption Procedure for Analysis of Metals in Atmospheric Particulate Matter, Environ. Sci. and Tech. 8(2):152, 1974.

6. Mitchell, W. J. and Midgett, M. R. A Means to Evaluate the Performance of Stationary Source Test Methods, Environ. Sci. and Tech. 10:85, 1976.

7. Federal Register, EPA Reference Methods 1, 2, 3, 4, and 5, 40 CFR 60, Appendix A, July 1983.

# APPENDIX A

# SAMPLING AND ANALYSIS PROCEDURES FOR THE DETERMINATION OF CADMIUM FROM COMBUSTION SOURCES

# APPENDIX A

## SAMPLING AND ANALYSIS PROCEDURES FOR THE DETERMINATION OF CADMIUM FROM COMBUSTION SOURCES

1. Principle and Applicability

1.1 Principle. Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principle components of the train include a high efficiency Whatman 934-AH® glass fiber filter and the impingers loaded with 5 percent nitric acid reagent. The filter is used to collect cadmium ladden particulate matter, and the 5 percent nitric acid will be used to determine if any cadmium passes through the filter.

Comprehensive chemical analyses of the collected samples are conducted to determine the concentration of the cadmium. This method can also be used for the determination of particulate loading.

1.2 Applicability. This method is applicable to the determination of cadmium emissions from cadmium sources. This method also may be used to determine particulate emission rates from stationary sources per U.S. EPA Method 5.[1]

1.3 Method Detection Limit. To be determined.

1.4 Method Accuracy and Precision. To be determined.

1.5 Interferences. To be determined.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 2-1. This sampling train configuration is adapted from EPA Method 5[1] procedures and as such, except for the impingers solution, the equipment required is identical to that used in EPA Method 5 determinations.

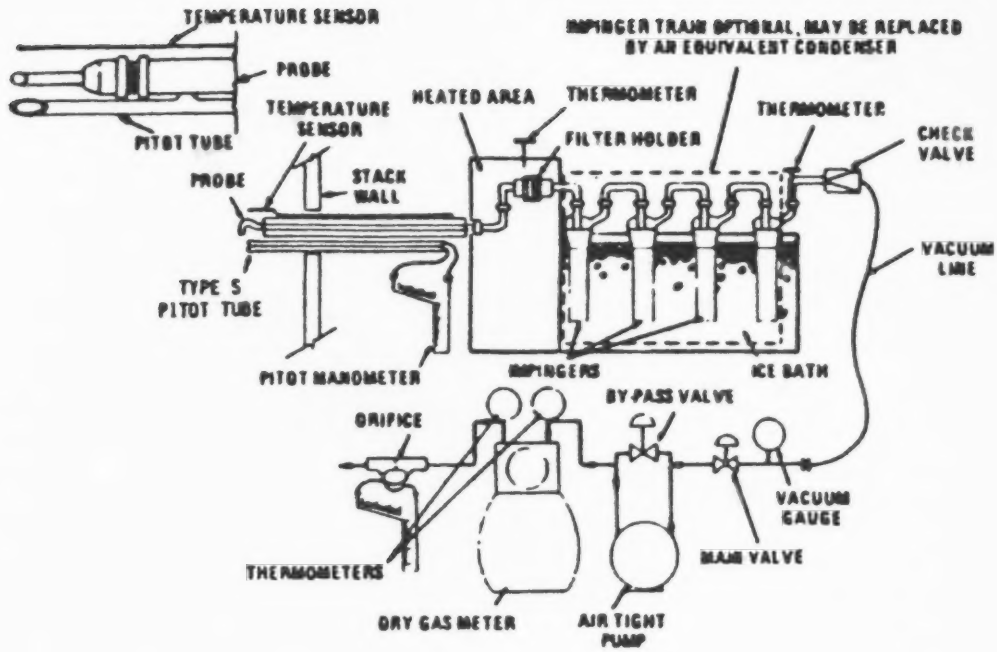


Figure 2-1. Cadmium train schematic diagram.

Construction details for the basic train components are given as part of EPA Method 5 in the report by Robert M. Martin;[4] commercial models of this equipment are also available. In addition, the following subsections list changes to the basic system described by Martin, and identify allowable train modifications.

Basic operating and maintenance procedures for the sampling train are described by Jerome J. Rom.[5] As correct usage is important in obtaining valid results, all users should refer to this reference and adopt the operating and maintenance procedures outlined therein, unless otherwise specified. The sampling train consists of the components described in the following paragraphs.

2.1.1 Probe Nozzle. Stainless steel (316) with a tapered leading edge of 30° and the taper shall be on the outside. The probe nozzle shall be the botton-hook or elbow design, unless otherwise necessary for a special application. The nozzle shall be constructed from seamless tubing.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.11 cm (1/8 to 7/16 in.) inside diameter. If higher volume sampling trains are used, nozzles with ID's increasing in increments of 0.16 cm (1/16 in.) can be procured. Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate glass or quartz tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F), or such other temperature appropriate for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to Martin[4] and utilizing the calibration curves of Rom[5] (or calibrated according to the procedure outlined in Rom) are considered acceptable.

Either borosilicate glass or quartz probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1,650°F) water-cooling of the stainless steel sheath is necessary, however, at

temperatures approaching and exceeding 500°C. The additional cooling of the probe liner is required at the higher temperatures to maintain the sample gas temperature below 135°C (275°F) at the filter.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of EPA Method 2[1] or other appropriate[7] devices. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2,[1] Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2[1].

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2[1]. One manometer shall be used for velocity head ($\Delta P$) readings, and the other for orifice differential pressure ($\Delta H$) readings.

2.1.5 Filter Holder. Borosilicate glass, with a filter support and a sealing gasket. The sealing gasket should be made of materials which will not introduce any material into the gas stream at the temperature at which the filter holder will be maintained. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The filter holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) in the vicinity of the filter holder during sampling.

2.1.7 Impinger Train. The following system shall be used to determine the stack gas moisture content; four 500 mL impingers connected in series with leak-free ground glass joints. All impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm. (1/2 in.) from the bottom of the outer cylinder. The first and second impingers shall contain known quantities of 5 percent nitric acid, the appropriate trapping solution, the third shall contain 2% potassium hydroxide to trap nitric acid, and the fourth shall contain a known weight of silica gel or equivalent desiccant.

2.1.8 Metering System. The necessary components are a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), and a dry gas meter capable of measuring volume to within 1 percent, as shown in Figure 2-1. At a minimum, the pump should be capable of 4 cfm free flow and the dry gas meter should have a recording capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 1 percent may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

Sampling trains utilizing metering systems designed for higher flow rates than those described by Martin[4] or Rom[5] may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm. Hg (0.1 in. Hg). The barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation difference between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m. (100 ft.) elevation increase or vice versa for elevation decrease.

2.1.10 Crushed Ice. Quantities ranging from 10-50 lb. may be necessary during a sampling run, depending upon ambient air temperatures.

2.1.11 Gas Density. The fixed gas samples for determining the stack gas density during the sampling run is taken using a Fyrite gas sampling train.

2.1.12 Calibration/Field Preparation Record. Documenting of the calibrations and preparation procedures (i.e. filter and silica gel tare weights, dry gas meter and thermocouple calibrations, etc.) is required.

2.2 Sample Collection Media

2.2.1 Filters. Glass or quartz fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.5 percent penetration) for 0.3 um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard

method D 2986-71.[3] Test data from the supplier's quality control program are sufficient for this purpose. In sources containing $SO_2$ or $SO_3$, the filter material must be of type that is unreactive to these acid gases.[2] Reeve Angel® 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

2.2.2 Silica Gel. Indicating type.

2.2.3 Impinger Solutions. Five percent nitric acid made with HPLC grade water shall be used to charge the first two impingers. The third impinger will contain 2% potassium hydroxide. 100 mL will be added to all three impingers. Additional details are found in Section 3.

2.3 Materials and Supplies Needed for Sample Recovery

2.3.1 Acetone. HPLC grade for probe and filter rinse recovery.

2.3.2 Five Percent Nitric Acid. Five percent nitric acid shall be used to aid in quantitatively transferring the impinger solutions that will be analyzed.

2.3.3 Probe Liner and Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of Teflon® or other inert material (nonmetallic) equal to the length of the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the nozzle, the cyclone, and the front of the filter housing.

2.3.4 Wash Bottles. Teflon® or glass wash bottles are required; polyethylene wash bottles may be used for the 5 percent nitric acid. However, they are not to be used with acetone.

2.3.5 Glass Sample Storage Containers. Chemically resistant, borosilicate clear glass bottles, 500 mL or 1,000 mL. Screw cap liners shall either be Teflon®-lined or otherwise constructed to be leak free and resistant to chemical attack by the acetone rinse solvent.

2.3.6 Petri Dishes. Glass, sealed around the circumference with wide (1 in.) Teflon® tape, for storage and transport of filter samples.

2.3.7 Graduated Cylinder and/or Triple-Beam Balance. To measure condensate water to the nearest 1 mL or 1 gram. Graduated cylinders shall have subdivisions no greater than 2 mL. Laboratory triple-beam balances capable of weighing to $\pm$0.5 gram are required.

2.3.8 Nalgene® Storage Containers. Screw cap polypropylene or polyethylene containers to contain the impinger solutions.

2.3.9 Funnels. Funnels may be required to aid in the recovery of samples for analyses.

2.4 Sample Preparation and Analysis

2.4.1 Preparation for Analysis. The preparation of all samples will result in a known volume in dilute nitric acid. The final sample volume will depend upon the concentration of cadmium in the samples. The concentrations must be within the linear range of the Atomic Absorption Spectrophotometer. The sensitivity of the AAS is approximately 0.03 µg/mL for 0.004 absorbance units. The linear upper level is approximately 2.0 µg/mL. Initially, the volume of each fraction will be measured and recorded in the analyst's notebook along with the Radian sample number and field identification.

2.4.2 Filter and Probe Rinses. The glass fiber filter from the EPA Modified Method 5 train will be Parr bombed with the dried probe rinses. The Parr bomb procedure will consist of placing the filter in a Teflon® cup, then transferring the probe fraction with 5 mL of $HNO_3$, followed by 5 mL of HF. The Teflon® cup is placed into the bomb and sealed. The Parr bomb is then placed into an oven at 100 to 150°C for 4 to 6 hours. The bomb is allowed to cool. The contents of the bomb are then rinsed with $HNO_3$ into a Nalgene volumetric flask and diluted to the desired volume.

2.4.3 Impinger Contents. The two impinger solutions containing 5 percent $HNO_3$ will be combined, and the total volume measured. The solution will be digested in $HNO_3$ and brought to a known volume.

2.4.4 Sample Analysis. The primary analytical measurement technique for cadmium in stack emission samples will be flame Atomic Absorption Spectrophotometry (AAS). Prior knowledge of the expected cadmium content will be helpful due to the limited linear range of the cadmium calibration curve of 2 µg/mL. The sensitivity of the flame AAS technique is 0.03 µg/mL. Knowledge of expected concentration in the stack emission samples will provide the approximate dilution or concentration step that will be required. The digested samples will be aspirated into the air/acetylene flame and the absorbance will be used to calculate the ppm

in each solution. The calibration curve constructed prior to sample analysis will be performed from working standards within the linear range of the instrument. The calibration curve will be plotted using the instrument software.

2.4.5 Atomic Absorption Conditions. The AAS wavelength will be set at 228.8 nm and the slit at 0.7 nm, as recommended in the instrument manual. The hollow cathode lamp will be optimized for maximum energy output. The air/acetylene flame and the burner head will be aligned for maximum absorbance using the 2 µg/mL standard.

2.4.6 Glassware and Plastic. All glassware and plastic is to be cleaned before use. The procedure is shown in Table 2-1.

2.4.6.1 Volumetric Flasks. 10-100 mL size. Used for preparing standards.

2.4.6.2 Funnels. Used for transferring samples.

2.4.6.3 Glasswool. Cleaned by 5 percent nitric acid triple rinse.

2.4.6.4 Miscellaneous Beakers. 10-400 mL size.

2.4.6.5 Disposable Pipets. For transferring sample to vials.

2.4.6.6 Graduated Cylinder. 100 and 500 mL size.

2.4.7 Drying Oven. Vacuum or convection type. 0-300°C.

2.4.8 Analytical Balance. Capable of weighing to the nearest 0.1 mg.

## 3. Reagents

Reagents should be screened for cadmium before use in either sampling or analytical procedures. Once a particular "lot" has been deemed acceptable by the established criteria, the same lot should be used to complete all analyses.

3.1 Solvents and Reagents. The solvents and reagents used for both the sampling and analysis should be screened prior to use regardless of the indicated purity. Solvents and reagents can be purchased and screened by "lot number" thus eliminating the necessity to screen each bottle. Solvents classified as "Distilled in Glass", "Pesticide Grade", "GC/MS Grade", etc. are generally free of most impurities.

Table 2-1.

| |
|---|
| 1. Hot soap and water wash. |
| 2. Tap water rinse. |
| 3. Five percent nitric acid rinse. |
| 4. Distilled deionized water rinse three times. |
| 5. Acetone rinse for and air dry. |

4. Procedure

4.1 Sampling.

4.1.1 Pretest Preparation. The complexity of this method is such that, in order to obtain reliable results, field personnel shall be trained in the use of the test procedures. All the components shall be maintained and calibrated according to the procedure described by Rom[5] unless otherwise specified.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass petri dishes) and keep the filters in these containers at all times except during sampling.

4.1.2 Preliminary Determination. Select the sampling site and the minimum number of sampling points according to EPA Method 1.[1] Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2.[1] It is recommended that a leak-check of the pitot lines (EPA Method 2,[1] Section 3.1) be performed. Determine the stack gas moisture content using the EPA Approximation Method 4[1] or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2,[1] Section 3.6. If the integrated EPA Method 3[1] sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with the sample run.

Select a nozzle size based on the range of preliminary gas stream velocity measurements so that it is not necessary to change the nozzle in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocities encountered; see Section 2.2 of EPA Method 2.[1]

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the probe.

Typically 30 dscf of sample volume is required for the determination of mass emission rates. Additional sample volume shall be collected as necessitated by analytical detection limit constraints.

Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate to the volume requirement. Allocate the same time to each traverse point as defined by EPA Method 1.[1] It is recommended that the length of time sampled at each traverse point be an integer or an integer plus one half minute to avoid time keeping errors.

4.1.3 Preparation of the Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is initiated.

Place 100 mL of 5 percent nitric acid in each of the first two impingers, 100 ml of 2 percent potassium hydroxide in the third impinger, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the silica gel plus impinger may be weighed together to the nearest 0.5 g and the weight recorded.

Using tweezers or clean disposable surgical gloves, place a labeled (identified) filter in the filter holder. Be sure that the filter is properly centered and the gasket placed to prevent the sample gas stream from bypassing the filter. Visually check the filter for holes or lifting after assembly is complete.

When glass liners are used, install the selected nozzle using a Viton-A O-ring if stack temperatures are less than 260°C (500°F) and a woven glass fiber gasket when temperatures are higher. See Rom[5] for details. Other connecting systems using either Teflon® or nylon ferrules may be used.

Set up the train as in Figure 2-1. If necessary, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to be great, to contain large particles, or when water droplets are present in the stack.

Connect all temperature sensors to an appropriate potentiometer/ display unit. Check all temperature sensors at ambient temperature.

Place crushed ice around the impingers. (This is better to do after the leak check.)

Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is required.

A lower vacuum may be used, provided that it is not exceeded during the test. Leak test by first plugging the inlet to the filter holder (cyclone, if applicable), evacuate to 280 mm. Hg (15 in. Hg) vacuum. Then the probe should be connected to the train and the train leak-checked at 25 mm. Hg (1 in. Hg) vacuum. Alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 280 mm. Hg (15 in. Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 $m^3$/min (0.02 cfm), whichever is less, is unacceptable and must be corrected.

These specific leak-testing instructions described in Rom[5] are strongly recommended. Start the pump with fine adjust valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the fine adjust valve until the desired vacuum is reached. Do <u>not</u> reverse direction of the fine adjust valve before unplugging system; this will cause water to back up into the filter or between the impingers. If the desired vacuum is exceeded, proceed as instructed below and begin again.

When the leak-check is completed, slowly remove the plug from the inlet.

4.1.4.2 Leak-Checks During Sampling Run. If during the sampling run, a component (e.g., filter assembly, impinger or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 except that it sha`l be done at a vacuum equal to or greater than the maximum value recorded at that point in the test. If

the leakage rate is found to be no greater than 0.00057 $m^3$/min (0.02 cfm) or 4 percent of the average sampling rate, the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall void the run unless it is impossible to repeat, in which case he/she shall record the leakage rate and plan to correct the sample volume as shown in Section 6.2 of this method. It should be noted that correction of the sample volume in this manner reduces the integrity of the pollutant concentrations data generated and should be avoided.

Immediately after a component change, and before sampling is re-initiated, a leak-check similar to a pretest leak-check must be conducted.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. Use the procedure outlined above insuring that the leak-check is conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. If the leakage rate is found to be not greater than 0.00057 $m^3$/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall attempt to repeat the run as previously discussed. If the run cannot be repeated, the tester shall record the leakage rate, correct the volume as shown in Section 6.2 of this method and shall consider the data obtained of questionable reliability.

4.1.5 Sample Collection. During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic. Maintain a gas temperature to the filter of 120 ± 14°C (248 ± 25°F).

For each run, record the data required on a data sheet. Take care to record the initial and final dry gas meter readings. Record the dry gas meter readings at the end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Level and zero the manometer initially and periodically throughout the sampling run.

Clean, the stack access ports prior to the test run to eliminate the possibility of sampling deposited material. To begin sampling, remove the nozzle covering, verify that the filter and probe heating

systems are at the specified temperature, and that the pitot tube and probe are properly positioned. Place the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. Rom[5] details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the stated ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.[6]

When the stack is under significant negative pressure (equivalent to the height of impinger stem) take care to turn the pump on at a low flow rate before inserting the probe into the stack.

When the probe is in position, block off the opening between the probe and stack access port to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by EPA Method 1.[1] Take care not to bump the probe nozzle into the stack walls when sampling near the walls or when removing and inserting the probe through the access port.

During the test run, make periodic adjustments to keep the temperature of the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the fourth impinger's outlet.

If the pressure drop across the filter becomes too high, making isokinetic sampling rates difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter holder assembly be used rather than attempting to change the filter itself. Before and after a new filter holder assembly is installed, conduct a leak-check.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or in cases where equipment failure necessitates a change of trains.

Note: When two or more trains are used, separate analysis of the front-half (if applicable) and impinger (if applicable) catches from each train should be performed, unless identical nozzle sizes were used on all trains. Then the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed.

At the end of the sample run, slowly open fine adjust valve and turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Leak-check the pitot lines as described in EPA Method 2,[1] Section 3.1. The lines must pass this leak-check in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinecity. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the results are acceptable.

4.2 Sample Recovery.

4.2.1 Disassembly of the Cadmium Train. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

4.2.1.1 When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling, as this will create a vacuum in the filter holder drawing water from the impingers back into the sorbent module.

Before moving the sampling train to the cleanup site, remove the probe from the sample train, and cap the open outlet, taking care not to lose any particulate that may be present. Cap the filter inlet. Remove the umbilical cord from the last impinger.

4.2.1.2 Cap the filter holder inlet and outlet. Ground glass stoppers, Teflon® caps or caps of other inert materials may be used to seal all openings.

4.2.1.3 Transfer the probe, the filter, and the impinger assembly to the clean-up area. This area should be clean and protected from the elements to minimize sample contamination or loss.

4.2.1.4 Save a portion of all washing solutions (acetone, 5 percent nitric acid) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle used and place them in separate, labeled glass sample containers for acetone/polyethylene for nitric acid.

4.2.1.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

4.2.2 Sample Handling and Transfer. Step-by-step sample handling and transfer procedures are outlined below. An example coding format for cadmium samples follows in Table 4-1.

4.2.3 Probe, Nozzle, Cyclone (if used), Filter Recovery.

4.2.3.1 Carefully remove the filter from the filter holder and place it in its identified petri dish. Use two pairs of tweezers to handle the filter. If it is necessary to fold the filter, insure that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, using a dry nylon bristle brush and/or a sharp-edged blade. Label the container and seal with wide (3/4 in.) Teflon® tape around the circumference of the lid.

4.2.3.2 Taking care to see that dust on the outside of the probe or other exterior surfaces does not contaminate the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe liner, and front half of the filter holder by washing these components with acetone into a glass container. Retain a solvent blank and analyze in the same manner as the samples. Perform rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent from a Teflon® wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particulate material. Make a final rinse of the inside surface with the solvent.

Have two people rinse the probe liner with the solvent by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A funnel (glass) may be used to aid in transferring liquid washes to the container.

Table 4-1. EXAMPLE CODING FORMAT FOR CADMIUM TRAIN SAMPLES

| Sample code | Container | Size | Sample description |
|---|---|---|---|
| CC | Glass | 100 mL, widemouth | Cyclone catch (if applicable) |
| PF-a,b,c.. | Glass petri dish(es) | 150 mm diameter | Particulate filter(s) |
| FHR | Glass | 1 L | Front-half rinse (acetone) |
| BHR | Plastic | 1 L | Impinger contents (5 percent nitric acid) plus back-half rinse |

Follow the solvent rinse with a brushing. Both persons should support the probe in an inclined position, while one sprays solvent into the upper end of the liner as he/she pushes the probe brush with a twisting action through the probe; the second person must place a sample container underneath the lower end of the probe, and catch any solvent and particulate matter which is brushed from the probe. Run the brush through the probe three or more times until no visible particulate material is carried out with the solvent or until none remains in the probe liner on visual inspection. Rinse the brush with solvent, and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe. Between sampling runs, keep brushes clean and protected from contamination.

4.2.3.3 Clean the inside of the front half of the filter holder and cyclone/ cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface at least three times to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if used). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected, tighten the sample container lid so that solvent will not leak out upon shipment to the laboratory. Mark the height of the fluid level to allow determination of whether or not leakage occurred during transport. Label the container clearly to identify its contents.

4.2.5 Silica Gel and Impingers Recovery.

4.2.5.1 Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may facilitate pouring the silica gel without losses. A rubber policeman may be used to aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids in the transfer. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

4.2.5.2 Recover the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±0.5 g by using a triple-beam balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Polyethylene containers are used for storage of the impinger catches.

4.2.6 Sample Preparation for Shipment. Prior to shipment, re-check all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon$^R$ tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

4.3 Sample Preparation for Analysis. The preparation of all samples will result in a known volume in dilute nitric acid. The final sample volume will depend upon the concentration of cadmium in the samples. Samples may be evaporated or diluted to concentrations within the linear range of the Atomic Absorption Spectrophotometer. The sensitivity of the AAS is approximately 0.03 ug/mL for 0.004 absorbance units. The upper limit of the linear range is approximately 2.0 ug/mL. Initially, the volume of each fraction will be measured and recorded in the analyst's notebook along with the Radian sample number and field identification.

4.3.1 Filter and Probe Rinses. The glass fiber filter from the EPA Modified Method 5 train will be Parr bombed with the dried probe rinses. The Parr bomb procedure will consist of placing the filter in a Teflon$^R$ cup, then transferring the probe fraction to the cup with 5 mL of $HNO_3$, followed by 5 mL of HF. The Teflon$^R$ cup is placed into the bomb and sealed. The Parr bomb is then placed into an oven at 100 to 150°C for 4 to 6 hours. The bomb is allowed to cool. The contents of the bomb are then rinsed with $HNO_3$ into a 50 mL Nalgene volumetric flask and diluted to exactly 50 mL.

4.3.2 Impinger Contents. The two impinger solutions containing 5 percent $HNO_3$ will be combined, and the total volume measured. The solution will be digested in $HNO_3$ and brought to a known volume.

4.4 Sample Analysis. The primary analytical measurement technique for cadmium in stack emission samples will be flame Atomic Absorption Spectrophotometry (AAS). Prior knowledge of the expected cadmium content will be helpful due to the limited linear range of the cadmium calibration curve of 2 µg/mL. The sensitivity of the flame AAS technique is 0.03 µg/mL. Knowledge of expected concentration in the stack emission samples will provide the approximate dilution required or concentration step needed. The digested samples will be aspirated into the air/acetylene flame and the absorbance will be used to calculate the ppm in each solution. The calibration curve constructed prior to sample analysis will be performed from working standards within the linear range of the instrument. The calibration curve will be plotted using the instrument software and plotter.

4.5 Atomic Absorption Conditions. The AAS wavelength will be set at 228.8 nm and the slit at 0.7 nm, as recommended in the instrument manual. The hollow cathode lamp will be optimized for maximum energy output. The air/acetylene flame and the burner head will be aligned for maximum absorbance using the 2 µg/mL standard.

4.6 Quantitation. Quantitation of each sample will be performed by constructing a working calibration curve by plotting the µg/mL (ppm) cadmium vs. absorbances. A minimum of two 4-point (including a blank) curves will be constructed to verify precision and stability prior to sample analysis. After sample analysis, the curve will be repeated to also verify curve stability. After every 10 samples, a sample of known concentration will be analyzed to verify instrument stability.

5. Calibration

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm. (0.001 in.). Measure the diameter of the nozzle face opening in 3 separate places (i.e. across 3 different diameters) and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm. (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube/Probe Assembly. The Type S pitot tube probe assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2,[1] or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented or corroded, and meets design and intercomponent spacing specifications.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in Rom.[5] It is recommended that a leak-check be conducted before calibrating the metering system. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. In these cases the following leak-check procedure is suggested: Make a 10-minute calibration run at 0.00057 $m^3$/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 $m^3$/min (0.02 cfm). Alternatively, the following procedure is suggested: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) of water by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in Rom.[5]

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in Rom.[5] Probes constructed according to Martin[4] need not be calibrated if the calibration curves in Rom[5] are used.

5.5 Temperature Gauges. Each thermocouple must be uniquely marked. All mercury-in-glass reference thermometers must conform to ASTM E-1 #63C or 63F specifications. Thermocouple should be calibrated in the laboratory without the use of extension leads. If extension leads are used in the fields, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5 percent.

5.5.1 Impinger and Dry Gas Meter Thermocouples. For the thermocouples used to measure the temperature of the dry gas meter, and the gas leaving the impinger train a two-point calibration at ice water, and room air temperatures is necessary. Accept the thermocouples only if the readings at both temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

5.5.2 Probe and Stack Thermocouple. For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water and hot oven temperatures must be performed; it is recommended that room air temperature be added. The thermometer and the thermocouple must agree to within 1.5 percent at each of the calibration points, a calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

5.6 Aneroid Barometer. Adjust the barometer initially and before each test program to agree to within ±2.5 mm Hg (0.1 in. Hg) of the mercury barometer, or the corrected barometric pressure value reported by a nearby National Weather Service station. (The NWS value must be at the same altitude above sea level or corrected.)

5.7 Triple-Beam Balance. Calibrate the triple beam balance before each test series using known weights; the weights must be within ±0.5 percent of the standards, or the balance adjusted to meet these limits.

6. Calculations

6.1 Nomenclature.

$A_n$ = Cross sectional area of nozzle, $m^2$ ($ft^2$).

$B_{ws}$ = Water vapor in the gas stream, proportion by volume.

$C_d$ = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

$L_a$ = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 $m^3$/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

$L_i$ = Individual leakage rate observed during the leak check conducted prior to the "i"$^{th}$ component change (i=1, 2, 3.....n) $m^3$/min (cfm).

$L_p$ = Leakage rate observed during the post-test leak check, $m^3$/min (cfm).

$M_d$ = Stack gas dry molecular weight, g/g-mole (lb/lb-mole).

$M_w$ = Molecular weight of water, 18.0 g/g-mole (18.0 lbs/lb-mole).

$P_{bar}$ = Barometric pressure at the sampling site, mm. Hg (in. Hg).

$P_s$ = Absolute stack gas pressure, mm. Hg (in. Hg).

$P_{std}$ = Standard absolute pressure, 760 mm. Hg (21.85 in. Hg).

R = Ideal gas constant, 0.06236 mm. Hg-$m^3$/°K-g-mole, (21.85 in. Hg-$ft^3$/°R-lb-mole).

$T_m$ = Absolute average dry gas meter temperature, °K (°R).

$T_s$ = Absolute average stack gas temperature, °K (°R).

$T_{std}$ = Standard absolute temperature, 293°K (528°R).

$V_{lc}$ = Total volume of liquid collected in the organic module condensate knockout trap, the impingers and silica gel, mL.

$V_m$ = Volume of gas sample as measured by dry gas meter, $m^3$ ($ft^3$).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

$v_s$ = Stack gas velocity, calculated by EPA Method 2,[1] Equation 2-9, using particulate field data, m/sec (ft/sec).

$Y$ = Dry gas meter calibration factor, dimensionless.

$\Delta H$ = Average pressure differential across the orifice meter, mm. $H_2O$ (in. $H_2O$).

$\rho_w$ = Density of water, 0.9982 g/mL (0.002201 lb/mL).

$\theta$ = Total sampling time, min.

$\theta_1$ = Sampling time interval, from the beginning of a run until the first component change, min.

$\theta_i$ = Sampling time interval between two successive component changes beginning with the interval between the first and second changes, min.

$\theta_p$ = Sampling time interval from the final ($n^{th}$) component change until the end of the sampling run, min.

13.6 = Conversion to mm. Hg (in. Hg) from mm. $H_2O$ (in. $H_2O$).

60 = Sec/min.

6.2 Dry Gas Volume at Standard Conditions. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm. Hg or 68°F, 29.92 in. Hg) by using the equation:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

where:

$K_1$ = 0.3858 °K/mm. Hg for metric units.

= 17.64 °R/in. Hg for English units.

Note: This equation can be used as written unless the leakage rate observed during any of the leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds $L_a$. If $L_p$ or $L_i$ exceeds $L_a$, the above equation must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace $V_m$ with the expression:

$$[V_m - \theta (L_p - L_a)]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace $V_m$ by the expression:

$$[V_m - \theta_1 (L_1 - L_a)] - \sum_{i=2}^{n} [\theta_i (L_i - L_a) - \theta_p (L_p - L_a)]$$

and substitute only those leakage rates ($L_i$ or $L_p$) which exceed $L_a$.

6.3 Moisture Content.

6.3.1 Volume of Water Vapor.

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc}$$

where:

$K_2$ = 0.001333 $m^3$/mL for metric units.
= 0.04707 $ft^3$/mL for English units.

6.4 Isokinetic Variation.

6.4.1 Calculation from Unreduced Data.

$$I = \frac{100 T_s [K_3 F_{lc} + (V_m/T_m) (P_{bar} + \Delta H/13.6)]}{60\theta V_s P_s A_n}$$

where:

$K_3$ = 0.003454 mm. Hg-$m^3$/mL-°K for metric units.
= 0.002669 in. Hg-$ft^3$/mL-°R for English units.

6.4.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60(1-B_{ws})}$$

$$= \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1-B_{ws})}$$

where:

$K_4$ = 4.320 for metric units.
= 0.09450 for English units.

6.4.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable.

6.5 Concentration of any Cadmium in the Emissions of a Combustion Process.

1) Multiply the concentration of the cadmium as determined in Section 4.6 by the final solution volume, typically 50 mL.

$C_{unk}$ (µg/mL) x sample volume (mL) =

amount (µg) of cadmium in sample

2) Sum the amount of cadmium found in all samples associated with a single train.

Total (µg) = (Probe rinse + filter (µg)) +

(Impingers + impinger rinse (µg))

3) Divide the total µg found by the volume of stack gas sampled ($m^3$).

Total µg/train sample volume =

concentration of cadmium (µg/$m^3$)

7. Quality Control.

Table 7-1 presents the major components of the quality control for this method.

7.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

7.2 Analysis. The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, and external performance tests. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective actions if problems are observed in laboratory operations or in field sampling activities.

Table 7-1. QUALITY ASSURANCE PROCEDURES FOR CADMIUM ANALYSIS

| | |
|---|---|
| Field blanks | 1 - Used flue gas sampling train per day (after recovery) |
| | 10% - Filter returned unused |
| | 1 - Field solvent blanks per lot |
| | 3 - Sample containers used |
| | 1 - Flue gas sampling train (before use, after lab cleaning) |
| Method blanks | 1 - Analytical method blank |
| Method validations | Method procedures studied and validated prior to initiating analysis program |
| Performance tests | Interlaboratory testing/split samples and/or performance audit samples |

7.2.1 Field Blanks. The field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents used. At a minimum, one complete used and recovered sampling train will be blanked. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

7.2.2 Method Blanks. A method blank from a clean and unused train must be made for each test program. This evaluates the contamination that can be derived from glassware, reagents, and handling before the start of testing.

7.2.3 Method Performance Evaluation. Evaluation of analytical procedures for cadmium must include the sample preparation procedures, and each associated analytical determination. The analytical procedures should be challenged by the test compounds.

7.3 Quantitative Analysis. Quantitative analytical methods are used to estimate the level of hazardous compounds in various matrices. The process of estimation or quantitation requires the precision, accuracy (bias), and detection limit of the analytical method to be known and documented.

7.3.1 Calibration.

1) Initial calibration standards are to be prepared and analyzed in the concentration series 0 (blank), X, 1.5X, and 2X where X is the concentration in the solvent being analyzed corresponding to the detection limit in the original matrix.

2) Daily Calibration. A minimum of two instrument calibration standards are to be run prior to analyses each day to establish that the sensitivity of the instrument has not changed over the working range from previous calibrations. The concentrations are to be distributed at a low, mid-level, and high level concentration. Data generated will be compared against the cumulative data to date to establish the stability of the instrument response. A mid-level calibration standard must be analyzed at the end of the day to establish that the instrument has not drifted during the course of analysis.

3) Quality control samples are to be inserted at random in a sample analysis series. At least one control sample is to be included with each lot of samples. The types of control samples are chosen to minimize the number of control samples and maximize the quality control data obtained from the analytical system.

4) Data generated from daily control samples are to be used to update control charts and, by addition to the existing data base, to refine the detection limit of the analytical method as well as the estimates of precision and accuracy.

5) Concentration values less than the average detection limit of the method will be reported as "less than" the detection limit unless sufficient data exists to justify a lower detection limit. Conversely, detection limits higher than the average detection limit (as is the case of a sample with high background interferences) will be reported as "less than" the higher detection limit.

References

1. Code of Federal Regulations. Title 40, Part 60, Appendix A, Methods 1-5.

2. Felix, L.G., G.I. Clinard, G.E. Lacey and J.D. McCain. Inertial Cascade Impactor Substrate Media for Flue Gas Sampling. Research Triangle Park, NC. Environmental Protection Agency, June 1977. PB-276 583/2BE, 83pp.

3. Gaseous Fuels: Coal and Coke - Atmospheric Analysis. Annual Book of ASTM Standards, Part 26, 1974, pp. 617-622.

4. Martin, R.M. Construction Details of Isokinetic Source - Sampling Equipment. Research Triangle Park, NC, Environmental Protection Agency, April, 1971. PB-203 060/BE, APTD-0581. 35 pp.

5. Rom, J.J. Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment. Research Triangle Park, NC. Environmental Protection Agency, March 1972. PB209 022/BE, APTD0576. 39 pp.

6. Shigehara, R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News Vol. 2, October 1974, pp. 4-11.

7. Vollaro, R.F. A Survey of Commerically Available Instrumentation for the Measurement of Low-Range Gas Velocities. Research Triangle Park, NC. Environmental Protection Agency, Emissions Measurement Branch, November 1976 (unpublished paper).

# APPENDIX B

## PROCEDURES USED TO ASSESS DATA PRECISION AND ACCURACY

APPENDIX B

PROCEDURES USED TO ASSESS DATA PRECISION AND ACCURACY

The main objective of this project is to assess the precision and accuracy of the proposed cadmium emission sampling and analysis system under field conditions. The viability of the proposed methods was evaluated in both field and laboratory experiments. Parameters that were investigated include the precision and accuracy of the sampling and analysis techniques, along with an assessment of the effect of sampling different total volumes.

The procedures that were implemented to assess the quality of 24 data points and associated measurements are discussed below.

B.1 DATA QUALITY ASSESSMENT

The experimental design (Section 6.0) allows the data to be grouped into sets that can be analyzed to evaluate precision and acuracy of data. The central tendency and dispersion of data are assessed by use of the following parameters.

- Arithmetic Mean - Offers average value of the measurement.

$$\bar{X} = \sum_{i=1}^{n} X_i/n$$

The average value, $\bar{X}$ obtained for a data set of n values gives the best representation of the measurement representation of the measurement, assuming that the differences between the individual values of $X_i$ are caused by random error.

Precision

- Standard Deviation - Offers the dispersion of a set of numbers about the mean value.

$$s = \left[\sum_{i=1}^{n} (X_i - X)^2/(n-1)\right]^{1/2}$$

or,

$$s = \left[\left(\Sigma X_1^2 - \Sigma X_1\right)^2/n\right)/(n-2)\Big]^{1/2}$$

- Coefficient of Variation - Normalizes the variability as a dimensionless quantity.

$$CV = s/X, \text{ or}$$

as a percentage

$$\% \text{ CV} = (s/X) \times 100.$$

Precision may be defined either in terms of standard deviation or as a coefficient of variation.

Accuracy

Accuracy is defined in terms of the bias, B, which is the difference (either on an absolute or percentage basis) between a measured value and an assumed "true" value. The larger the difference, the lower the accuracy.

$$B = X - T, \text{ or}$$

$$\% \text{ B} = \frac{X-T}{T} \cdot 100$$

## B.2 ANALYSIS OF VARIANCE OF TEST RESULTS

Field Test No. 1

Table B-1 gives the test configuration for the first field study results on the analysis of cadmium. An analysis of variance was done to investigate any effects due to sample trains used, and effects due to the test day and time of day (a.m. or p.m.). It is clear by examination of Table 6-1 that if Test No. 1, the morning of the first day, were used, there would be a "day" effect, because the ug/dscm is about 2.5 times less than the results from tests 2 through 6. The model[a] used for this analysis was:

$$CD = u + \text{Train} + \text{TOD} + \text{Day} + \text{Error}, \qquad \text{(B-1)}$$

[a]Hicks, Charles R. "Fundamental Concepts in the Design of Experiments," Holt, Reinhart and Winston, New York (1964).

Table B-1. TEST CONFIGURATION

| | AM | | | | PM | | | |
|---|---|---|---|---|---|---|---|---|
| Day 1 | | | | | | | | |
| Time, min | 130 | 130 | 130 | 130 | 65 | 65 | 65 | 65 |
| Train | A | B | C | D | A | B | C | D |
| Flow, dscm | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Volume, dscm | 65 | 65 | 65 | 65 | 32.5 | 32.5 | 32.5 | 32.5 |
| Test No. | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| Day 2 | | | | | | | | |
| Time, min | 70 | 70 | 70 | 70 | 130 | 130 | 130 | 130 |
| Train | A | B | C | D | A | B | C | D |
| Flow, dscm | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Volume, dscm | 35 | 35 | 35 | 35 | 65 | 65 | 65 | 65 |
| Test No. | 3 | 3 | 3 | 3 | 4 | 4 | 4 | 4 |
| Day 3 | | | | | | | | |
| Time, min | 130 | 130 | 130 | 130 | 70 | 70 | 70 | 70 |
| Train | A | B | C | D | A | B | C | D |
| Flow, dscm | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Volume, dscm | 65 | 65 | 65 | 65 | 35 | 35 | 35 | 35 |
| Test No. | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 6 |

where

CD = cadmium concentration in ug/dscm,

$u_1$ = overall mean of CD for Field Test No. 1 = 92.4

Train = four trains used - A, B, C, and D

TOD = time of day, a.m. or p.m.

Day = day, Day 1, Day 2, and Day 3.

The analysis of variance (ANOVA) table is given in Table B-2 for the Field Study results. The ANOVA results indicate that none of the independent variables, Train, TOD, Day significantly affected the cadmium concentration, CD. These conclusions may be drawn by examining the P values in Table B-2. The P values give the probability that the effect listed under the "Source" column is zero.

The usual (see Hicks' reference, op. cit.) criterion for significance is the 0.05 level, called the level of significance. If $P \leq 0.05$ then the effect is taken to be significant and there is a 95% (or greater) probability that the effect is not zero.

Table B-3 contains the raw analytical data from the calibration curves for ICAP and AA,and done for Field Test No. 1.

Field Test No. 2

Table B-4 gives the test configuration for the second field study results on the analysis of cadmium. Only four runs were involved for the second field test. In the first field test six tests were run, one each morning and afternoon for three days. Because the "day" effect, and "time-of-day" effect was not significant or of importance in the first field test, a different model was chosen for the analysis of variance (ANOVA) for the second field test. The model chosen was:

$$CD = U_2 + Run + Train + Error$$

where

CD = cadmium concentration in mg/dscm

$U_2$ = overall mean of CD for Field Test No. 2

Run = run numbers, 1, 2, 3, or 4

Train = quad-train designation, A, B, C, or D, and

Error = residual unassigned effect

Table B-2. ANALYSIS OF VARIANCE OF FIELD STUDY RESULTS

DEP VAR: CD N: 19 MULTIPLE R: .451 SQUARED MULTIPLE R: .203

Analysis of Variance

| Source[a] | Sum-of-Squares | DF | Mean-Square | F-Ratio | P |
|---|---|---|---|---|---|
| TRAIN | 333.209 | 3 | 111.070 | .560 | .651 |
| TOD | 21.713 | 1 | 21.713 | .110 | .746 |
| DAY | 283.296 | 2 | 141.648 | .715 | .509 |
| ERROR | 2377.977 | 12 | 198.165 | | |

[a]Did not use the results of Test No. 6 for Train B, which was declared an outlier; see Table 6-1.

Table B-3. RAW ANALYTICAL DATA FROM THE CALIBRATION CURVES

Atomic Absorption Spectrophotometry

| | Set A | Set B | Set C | Set D |
|---|---|---|---|---|
| Blank | 0.0010 Abs. | 0.0010 | 0.0010 | 0.0010 |
| 0.10 ug/mL | 0.0205 | 0.0190 | 0.0190 | 0.0190 |
| 1.00 | 0.1745 | 0.1790 | 0.1770 | 0.1770 |
| 2.00 | 0.3305 | 0.3330 | 0.3355 | 0.3415 |
| Correlation: | 0.99964 | 0.99931 | 0.99964 | 0.99985 |
| Slope: | 0.16472 | 0.16667 | 0.16767 | 0.17049 |
| Intercept: | 0.00397 | 0.00383 | 0.00318 | 0.00249 |

| Correlation: | | Slope: | |
|---|---|---|---|
| Mean | 0.99961 | Mean | 0.16739 |
| Std. Dev. | 0.00022 | St. Dev. | 0.00240 |
| CV | 0.02% | CV | 1.43% |

Inductively Coupled Argon Plasma

| | Set A | Set B | Set C | Set D |
|---|---|---|---|---|
| Blank | 200 Em. Uts. | 321 | 158 | -73 |
| 0.10 ug/mL | 1386 | 1842 | 1720 | 1717 |
| 1.00 | 14025 | 14372 | 14058 | 13945 |
| 2.00 | 27529 | 27325 | 27708 | 27939 |
| Correlation: | 0.99995 | 0.99979 | 0.99998 | 0.99992 |
| Slope: | 13725 | 13505 | 13738 | 13906 |
| Intercept: | 148 | 498 | 264 | 105 |

| Correlation: | | Slope: | |
|---|---|---|---|
| Mean | 0.99991 | Mean | 13718 |
| Std. Dev. | 0.00008 | Std. Dev. | 164 |
| CV | 0.008% | CV | 1.2% |

Note: ICAP values are expressed in Emission Units.

Table B-4. TEST CONFIGURATION FOR THE SECOND CADMIUM SAMPLING FIELD TEST*

| | | 2-Hour Train | | | | 1-Hour Train | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | A | B | C | D |
| Day 1 | Target Time, mins | 120 | 120 | 120 | 120 | | | | |
| | Actual time, mins | 120 | 120 | 120 | 120 | | | | |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | | | | |
| | Actual sample volume, DSCF | 59.1 | 59.2 | 63.3 | 62.1 | | | | |
| Day 2 | Target time, mins | 120 | 120 | 120 | 120 | 60 | 60 | 60 | 60 |
| | Actual time, mins | 120 | 120 | 120 | 120 | 60 | 60 | 60 | 60 |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | 30 | 30 | 30 | 30 |
| | Actual sample volume, DSCF | 74.2 | 73.5 | 78.8 | 76.3 | 30.2 | 30.2 | 32.3 | 31.4 |
| Day 3 | Target time, mins | 120 | 120 | 120 | 120 | | | | |
| | Actual time, mins | 118.5 | 118.5 | 118.5 | 118.5 | | | | |
| | Desired sample volume, DSCF | 60 | 60 | 60 | 60 | | | | |
| | Actual sample volume, DSCF | 60.4 | 60.0 | 64.3 | 63.3 | | | | |

*Isokinetic flowrates were maintained at nominally, 0.5 DSCFM.

The data input to the ANOVA were the cadmium concentrations in mg/dscm from Table 11. Table B-5 gives the ANOVA table for this analysis and shows that run number is a significant factor, while trains is not at the 0.05 level of significance. This result was expected and the data confirm these expectation. Thus, the cadmium concentration is not a function of a particular sample train, while it is a function of the run number. Since there was no control on the feedstock to the incinerator, it is to be expected that the cadmium level should be a function of the run number.

Table B-5. ANOVA TABLE, SECOND CADMIUM SAMPLING FIELD TEST

| Source of Variation | V, df | Sum of Squares | Mean Square | F Statistic | $F_{V_1, V2, 0.95}$ |
|---|---|---|---|---|---|
| Run | 3 | 0.1131 | 0.0377 | 37.0250 | 5.08 |
| Train | 3 | 8.167635e-3 | 2.722545e-3 | 2.6731 | 5.08 |
| Error | 9 | 9.166480e-3 | 1.018498e-3 | | |
| Total | 15 | 0.1305 | | | |

# APPENDIX C

## SITE SPECIFIC SYSTEMS AUDIT CHECKLIST
## CADMIUM SAMPLING/ANALYSIS PROGRAM

SITE SPECIFIC SYSTEMS AUDIT CHECKLIST
CADMIUM SAMPLING/ANALYSIS PROGRAM

SITE: DATE: 10/28/85 - 11/1/85

PROJECT: Cadmium Method Validation AUDITOR: Blake Bath (On-Site QC Monitor)

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| | | | PROJECT ORGANIZATION AND PERSONNEL |
| X | | | 1. EPA Project Officer: Thomas E. Ward |
| X | | | 2. Radian Project Director: Bob Moseman |
| X | | | 3. Field Sampling Manager: Jim McReynolds |
| X | | | 4. Field Sample Custodian: Blake Bath |
| X | | | 5. On-Site QC Monitor: Blake Bath |
| X | | | 6. All field personnel trained in the use of the test procedures. |
| | | | SAFETY |
| X | | | 1. All Radian personnel wear hard hats, safety glasses, and safety shoes while on-site. |
| X | | | 2. Ear plugs and respirators available. |
| X | | No requests were made. | 3. Radian personnel follow all safety requests made by plant. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| | | | PRE-TEST PREPARATION |
| X | | Done prior to train assembly | 1. Silica gel pre-weighed (200-300g portions), sealed in air-tight containers to the nearest 0.5 g. (or just prior to train assembly) |
| X | | | 2. Filters checked visually against light. |
| X | | | 3. Shipping containers (glass petri dishes) labelled properly. |
| X | | | 4. Filters kept in containers at all times except during sampling. |
| | | | PRELIMINARY DETERMINATIONS |
| X | | | 1. Stack Pressure, temperature, and range of velocity heads determined using EPA Method 2. |
| X | | | 2. Pilot lines leak-checked |
| X | | | 3. Stack gas moisture content determined (using EPA Method 4). |
| X | | | 4. Stack gas dry molecular weight determined (EPA Method 3), with integrated bag sample taken simultaneously with the sample run. |
| X | | | 5. Nozzle size properly selected (to maintain isokinetic sampling rate). Minimum sample volume (30, 45, or 60) exceeded. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | | | 6. Proper differential pressure gauge chosen. |
| X | | As needed. | 7. Suitable probe liner and probe length selected (to sample all traverse points). |
| X | | | 8. Length of total sampling time determined. |
| | | | SAMPLING TRAIN PREPARATION |
| X | | All sealed until just prior to sampling. | 1. All openings covered until just prior to assembly or until sampling. |
| X | | During Run #5, the #1 and #2 impingers contained distilled water (per request of Tom Ward). | 2. Impingers prepared as follows:<br>#1 - 100 ml of 5% nitric acid<br>#2 - 100 ml of 5% nitric acid<br>#3 - Empty<br>#4 - 200-300 grams silica gel |
| X | | | 3. Filter labeled and placed in filter holder using tweezers or clean disposable surgical gloves. |
| X | | | 4. Filter visually checked for holes or lifting following assembly. |
| X | | Teflon ferrules | 5. Installation of nozzle using woven glass fiber gasket (500°F). |
| X | | Micromite. | 6. All temperature sensors connected to appropriate potentiometer/display unit. |
| X | | | 7. All temperature sensors checked at ambient temperature. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | ____ | Impinger exit temp below 70°F. | 8. Crushed ice placed around impingers following leak check. |
| X | ____ | | 9. Filter and probe heating systems turned on and set at desired operating temperatures. Temperatures allowed to stabilize. |
| | | | PRE-TEST LEAK-CHECK PROCEDURES |
| X | ____ | | 1. Leak test conducted according to correct procedures. (Plug inlet to filter holder, evacuate to 280 mm/hg vacuum, connect probe to train and leak check at 25 mm. Hg vacuum.) |
| X | ____ | | 2. Leak-check entire train in one step, at 280 mm/hg vacuum. |
| X | ____ | | 3. Leakage rate $\leq$ 4% of the average sampling rate. |
| | | | SAMPLE COLLECTION PROCEDURES |
| X | ____ | | 1. Isokinetic sampling rate $\pm$ 10% of true isokinetic maintained during each run. |
| X | ____ | | 2. Gas temperature passing through filter maintained at 120 $\pm$ 14°C (248 $\pm$ 25°F) during run. |
| X | ____ | | 3. Initial and final dry gas meter readings recorded at the following times:<br>- end of each sampling time increment<br>- when flow rate changes made<br>- before and after each leak-check<br>- after sampling stops. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | | | 4. Manometer leveled and zeroed initially and periodically throughout each sampling run. |
| X | | | 5. Stack Access ports cleaned prior to each test run. |
| X | | | 6. Nomographs used to adjust isokinetic sampling rate. |
| | N/A | | 7. Stack Traversing as required. |
| X | | | 8. Temperature at 4th impinger's outlet maintained at $\leq 20^{\circ}C$ ($68^{\circ}F$). |
| X | | | 9. If filter needs replacing during sample run, use another complete filter holder assembly rather than changing the filter itself. |
| X | | | 10. Conduct leak-check before and after a new filter holder assembly is installed. |
| X | | | 11. Use only one train for an entire sample run when required. |
| | | | LEAK-CHECKS DURING SAMPLING |
| | N/A | There were no component changes during a run. | 1. Conduct leak-check if any components need changing during a test run:<br>- filter assembly<br>- impinger<br>- sorbent trap |
| | N/A | | 2. Conduct leak-check immediately after a component change and before sampling is re-initiated. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| | | | POST-TEST LEAK CHECKS |
| X | | | 1. Conduct a post-test leak check at a vacuum equal to or greater than the maximum value recorded during the sampling run. |
| X | | | 2. Acceptance criteria met. |
| | | | CADMIUM TRAIN DISASSEMBLY |
| X | | | 1. Probe allowed to cool down at the end of sampling period. |
| X | | | 2. Probe tip wiped off and capped properly. |
| X | | | 3. Filter inlet/outlet capped properly. |
| X | | | 4. Ground glass stoppers, Teflon caps or other appropriate material used to seal all openings. |
| X | | | 5. Probe, Filter, and impinger assembly transferred to clean-up area. |
| X | | | 6. Inspect train prior to and during disassembly. |
| | | | SAMPLE RECOVERY |
| | | | Filters |
| X | | | 1. All filter fibers, etc. transferred using a dry nylon bristle brush and/or sharp-edged blade. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | | | 2. All glass filter sample containers labelled and sealed with wide Teflon tape around the lid. |
| | | | Probe |
| X | | | 3. Probe nozzle, probe liner, and front half of filter holder recovered with acetone. This rinse collected in a glass container. |
| X | | Retained. | 4. Solvent blanks retained and analyzed with samples. |
| X | | | 5. Rinses performed as specified in the method. (2 persons, etc.) |
| X | | | 6. All brushes kept clean and protected from contamination between sampling runs. |
| | | | Impingers |
| X | | | 7. Color of silica gel noted. |
| X | | | 8. Silica gel transferred to appropriate container and sealed. |
| X | | | 9. Silica gel transferred without using water or other liquids. |
| X | | * During Run #4 Train A impingers contained some cream-colored particulate, indicating the presence of excess materials. This train was recovered according to the regular procedures. | 10. Container and its contents weighed. |
| X | | | *11. Impingers recovered properly, according to method. |
| X | | | *12. Impinger catches stored in polyethylene containers. |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| | | | DOCUMENTATION |
| X | | | 1. Chain-of-custody documentation completed for each component of the trains. |
| X | | All information recorded in logbook. | 2. Date and pertinent observations properly recorded. |
| X | | | 3. Trouble-shooting procedures documented. |
| X | | | 4. Procedural changes documented. |
| X | | | 5. Equipment/Instrument modifications documented. |
| | | | QUALITY CONTROL PROCEDURES<br>Sample Prep for Shipment |
| X | | | 1. All sample containers re-checked to ensure caps are well-secured. |
| X | | | 2. All container lids sealed with Teflon tape. |
| X | | Shipped by car. | 3. All liquids shipped upright. |
| X | | | 4. All particulate filters shipped with particulate catch facing upward. |
| | | | Blanks |
| X | | Two trains blanked for the 3-day test period. | 1. Field Blanks:<br>- one used flue gas sampling train per day (after recovery)<br>- 10% filters returned unused<br>- 1 solvent blank per lot<br>- 3 sample containers used<br>- 1 flue gas sampling train (before use, after lab cleaning) |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | | | 2. One analytical Method blank from a clean and unused train. |
| | | | Calibration |
| X | | | 1. Probe nozzle calibrated before use in the field. (permanently and uniquely identified) |
| X | | | 2. Pilot Tube/Probe Assembly calibrated properly (coefficient of 0.84). |
| X | | | 3. Metering System properly calibrated;leak-checked, before and after each field use. |
| X | | | 4. Probe Heater calibrated properly. |
| X | | Readouts calibrated. | 5. Temperature gauges thermocouples calibrated in laboratory. |
| X | | | 6. Impinger and Dry Gas Meter Thermocouples calibrated using a 2-point calibration at ice water and room air temperatures. (Agreement of ± 2% (3.6°F) with absolute valve of the reference thermometer. |
| X | | | 7. Probe and Stack Thermocouples calibrated using a 3-point calibration at ice water, boiling water, and hot oven temperatures. (Agreement ± 1.5% at each calibration point). |

| YES | NO | COMMENTS | ITEM |
|---|---|---|---|
| X | ____ | | 8. Aneroid Barometer calibrated to agree within ± 2.5 mm Hg of mercury barometer. (or connected barometric pressure valve reported by a nearby National Weather Service Station.) |
| X | ____ | Mettler balance. | 9. Triple-Beam Balance calibrated using known weights. ( ± 0.5% agreement with standards). |

# APPENDIX D

## FIELD TEST PROGRAM DATA

D-1 Example Calculations Test No. 1 and Test No. 2
Definition of Terms

D-2 Calculated Results for Cadmium and Particulates

# APPENDIX D-1

## EXAMPLE CALCULATION - DEFINITION OF TERMS

# RADIAN SOURCE TEST
# EPA METHODS 2-5
# DEFINITION OF TERMS

| PARAMETER | DEFINITION |
|---|---|
| Tt(min.) | TOTAL SAMPLING TIME |
| Dn(in.) | SAMPLING NOZZLE DIAMETER |
| Ps(in.H2O) | ABSOLUTE STACK STATIC GAS PRESSURE |
| Vm(cu.ft.) | ABSOLUTE VOLUME OF GAS SAMPLE MEASURED BY DGM |
| Vw(gm.) | TOTAL STACK MOISTURE COLLECTED |
| Pm(in.H2O) | AVERAGE STATIC PRESSURE OF DGM |
| Tm(F) | AVERAGE TEMPERATURE OF DGM |
| Pb(in.Hg.) | BAROMETRIC PRESSURE |
| % CO2 | CARBON DIOXIDE CONTENT OF STACK GAS |
| % O2 | OXYGEN CONTENT OF STACK GAS |
| % N2 | NITROGEN CONTENT OF STACK GAS |
| SQR(DELPS) | AVE. SQ. ROOT OF S-PITOT DIFF. PRESSURE-TEMP. PRODUCTS |
| As(sq.in.) | CROSS-SECTIONAL AREA OF STACK(DUCT) |
| Ts(F) | TEMPERATURE OF STACK |
| Vm(dscf) | STANDARD VOLUME OF GAS SAMPLED ,Vm(std),AS DRY STD. CF |
| Vm(dscm) | STANDARD VOLUME OF GAS SAMPLED,Vm(std),AS DRY STD. CM |
| Vw gas(scf) | VOLUME OF WATER VAPOR IN GAS SAMPLE,STD |
| % moisture | WATER VAPOR COMPOSITION OF STACK GAS |
| Md | PROPORTION, BY VOLUME,OF DRY GAS IN GAS SAMPLE |
| MWd | MOLECULAR WEIGHT OF STACK GAS,DRY BASIS LB/LB-MOLE |
| MW | MOLECULAR WEIGHT OF STACK GAS,WET BASIC LB/LB-MOLE |
| Vs(fpm) | AVERAGE STACK GAS VELOCITY |
| Flow(acfm) | AVERAGE STACK GAS FLOW RATE(ACTUAL STACK COND.) |
| Flow(acmm) | AVERAGE STACK GAS FLOW RATE(ACTUAL STACK COND.) |
| Flow(dscfm) | AVERAGE STACK GAS VOLUMETRIC FLOW RATE(DRY BASIS) |
| Flow(dscmm) | AVERAGE STACK GAS VOLUMETRIC FLOW RATE(DRY BASIS) |
| % I | PERCENT ISOKINETIC |
| % EA | PERCENT EXCESS AIR IN STACK GAS |
| DGM | DRY GAS METER |
| Y | DRY GAS METER CORRECTION FACTOR |
| Pg | STACK STATIC GAS PRESSURE |
| Cp | PITOT COEFFICIENT |
| dH | ORIFICE PLATE DIFF. PRESS. VALUE |
| dP | PITOT DIFF. PRESS. VALUE |
| *** EPA STANDARD CONDITIONS | Temperature = 68 deg-F (528 deg-R)<br>Pressure = 29.92 in. Hg. |

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  2 - 5
S A M P L E  C A L C U L A T I O N

| | |
|---|---|
| PLANT | : CADMIUM VALIDATION TEST |
| PLANT SITE | : --- , |
| SAMPLING LOCATION | : #1 ESP OUTLET |
| TEST # | : 1-A |
| DATE | : 10/29/85 |
| TEST PERIOD | : 1005-1215 |

1) Volume of dry gas sampled at standard conditions (68 deg-F ,29.92 in. Hg).

$$Vm(std) = \frac{Y \times Vm \times [T(std) + 460] \times [Pb + (Pm/13.6)]}{P(std) \times (Tm + 460)}$$

$$Vm(std) = \frac{.9972 \times 66.819 \times 528 \times [30.24 + (.84/13.6)]}{29.92 \times (76.7 + 460)}$$

$$Vm(std) = 66.388 dscf$$

2) Volume of water vapor at standard conditions:

$$Vw(gas) = 0.04715\ cf/gm \times W(l)\ gm$$

$$Vw(gas) = 0.04715 \times 181.2 = 8.544\ scf$$

3) Percent Moisture in stack gas :

$$\%M = \frac{100 \times Vw(gas)}{Vm(std) + Vw(gas)}$$

$$\%M = \frac{100 \times 8.544}{66.388 + 8.544} = 11.40\ \%$$

4) Mole fraction of dry stack gas :

$$Md = \frac{100 - \%M}{100} = \frac{100 - 11.40}{100} = .8859819$$

# SAMPLE CALCULATION
## PAGE TWO

5)Average Molecular Weight of DRY stack gas :

MWd = (.44 x %CO2) + (.32 x %O2) + (.28 x %N2)

MWd = (.44 x 6.5 ) + (.32 x 11.5 ) + (.28 x 82 ) = 29.5

6)Average Molecular Weight of wet stack gas :

MW = MWd x Md + 18(1 - Md)

MW = 29.5 x .8859819 + 18(1 - .8859819 ) = 28.18879

7) Stack gas velocity in feet-per-minute (fpm) at stack conditions :

Vs = KpxCp x [SQRT (dP)](ave) x SQRT [Ts (avg)] x SQRT [1/(PsxMW)] x 60sec/min

Vs = 85.49 x .84 x 60 x 19.488 x SQRT[1/( 29.94588 X 28.18879 )]

Vs = 2890.058 FPM

8) Average stack gas dry volumetric flow rate (DSCFM) :

$$Qsd = \frac{Vs \times As \times Md \times T(std) \times Ps}{144 \text{ cu.in./cu.ft.} \times (Ts + 460) \times P(std)}$$

$$Qsd = \frac{2890.058 \times 9424 \times .8859819 \times 528 \times 29.94588}{144 \times 907.9 \times 29.92}$$

Qsd = 97538.38 dscfm

## SAMPLE CALCULATION
## PAGE THREE

9)Isokinetic sampling rate (%) :

Dimensional Constant C = K4 x 60 x 144 x [1 / (P1 /4)]
K4 = .0945 FOR ENGLISH UNITS

$$I\% = \frac{C \times Vm(std) \times (Ts + 460)}{Vs \times Tt \times Ps \times Md \times (Dn)^2}$$

$$I\% = \frac{1039.574 \times 66.3882 \times 907.9}{2890.058 \times 130 \times 29.94588 \times .8859819 \times ( .248 )^2}$$

I% = 102.2044

10) Excess air (%) :

$$EA = \frac{100 \times \%O2}{(.264 \times \%N2) - \%O2} = \frac{100 \times 11.5}{(.264 \times 82 ) - 11.5}$$

EA = 113.32

11) Particulate Concentration :

Cs = ( grams part.) / Vm(std) = .0000605 / 66.3882

Cs = 0.0000009 Grams/DSCF

$$Ca = \frac{T(std) \times Md \times Ps \times Cs}{P(std) \times Ts}$$

$$Ca = \frac{528 \times .8859819 \times 29.94588 \times 0.0000009}{29.92 \times 907.9}$$

Ca = 0.0000005 Grams/ACF

LBS/HR = Cs x 0.002205 x Qsd x 60

LBS/HR = 0.0000009x 0.002205 x 97538.4 x 60

LBS/HR = .0117598

Program Revision:1/16/84

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  2 - 5
S A M P L E  C A L C U L A T I O N

| | |
|---|---|
| PLANT | : CADMIUM #2 |
| PLANT SITE | : |
| SAMPLING LOCATION | : STACK EXHAUST |
| TEST # | : CAD 1-A |
| DATE | : 7/23/86 |
| TEST PERIOD | : (1605-1651) (1656-1810) |

1) Volume of dry gas sampled at standard conditions (68 deg-F ,29.92 in. Hg).

$$Vm(std) = \frac{Y \times Vm \times [T(std) + 460] \times [Pb + (Pm/13.6)]}{P(std) \times (Tm + 460)}$$

$$Vm(std) = \frac{1.003 \times 66.162 \times 528 \times [29.41 + (.95/13.6)]}{29.92 \times (124.4 + 460)}$$

$$Vm(std) = 59.074 dscf$$

2) Volume of water vapor at standard conditions:

$$Vw(gas) = 0.04715 \text{ cf/gm} \times W(1) \text{ gm}$$

$$Vw(gas) = 0.04715 \times 170.1 = 8.020 \text{ scf}$$

3) Percent Moisture in stack gas :

$$\%M = \frac{100 \times Vw(gas)}{Vm(std) + Vw(gas)}$$

$$\%M = \frac{100 \times 8.020}{59.074 + 8.020} = 11.95 \%$$

4) Mole fraction of dry stack gas :

$$Md = \frac{100 - \%M}{100} = \frac{100 - 11.95}{100} = .8804636$$

# SAMPLE CALCULATION
## PAGE TWO

5)Average Molecular Weight of DRY stack gas :

MWd = (.44 x %CO2) + (.32 x %02) + (.28 x %N2)

MWd = (.44 x 5.5 ) + (.32 x 15.5 ) + (.28 x 79 ) = 29.5

6)Average Molecular Weight of wet stack gas :

MW = MWd x Md + 18(1 - Md)

MW = 29.5 x .8804636 + 18(1 - .8804636 ) = 28.12533

7) Stack gas velocity in feet-per-minute (fpm) at stack conditions :

Vs = KpxCp x [SQRT (dP)](ave) x SQRT [Ts (avg)] x SQRT [1/(PsxMW)] x 60sec/min

Vs = 85.49 x .84 x 60 x 13.88235 x SQRT[1/( 29.41368 X 28.12533 )]

Vs = 2079.627 FPM

8) Average stack gas dry volumetric flow rate (DSCFM) :

$$Qsd = \frac{Vs \times As \times Md \times T(std) \times Ps}{144 \text{ cu.in./cu.ft.} \times (Ts + 460) \times P(std)}$$

$$Qsd = \frac{2079.627 \times 754.7695 \times .8804636 \times 528 \times 29.41368}{144 \times 601.75 \times 29.92}$$

Qsd = 8278.549 dscfm

# SAMPLE CALCULATION
# PAGE THREE

9)Isokinetic sampling rate (%) :

Dimensional Constant C = K4 x 60 x 144 x [1 / (Pi /4)]
K4 = .0945 FOR ENGLISH UNITS

$$I\% = \frac{C \times Vm(std) \times (Ts + 460)}{Vs \times Tt \times Ps \times Md \times (Dn)^2}$$

$$I\% = \frac{1039.574 \times 59.07409 \times 601.75}{2079.627 \times 120 \times 29.41368 \times .8804636 \times ( .247 )^2}$$

I% = 93.72329

10) Excess air (%) :

$$EA = \frac{100 \times \%O2}{(.264 \times \%N2) - \%O2} = \frac{100 \times 15.5}{(.264 \times 79 ) - 15.5}$$

EA = 289.40

11) Particulate Concentration :

Cs = ( grams part.) / Vm(std) = .001459 / 59.07409

Cs = 0.0000247 Grams/DSCF

$$Ca = \frac{T(std) \times Md \times Ps \times Cs}{P(std) \times Ts}$$

$$Ca = \frac{528 \times .8804636 \times 29.41368 \times 0.0000247}{29.92 \times 601.75}$$

Ca = 0.0000188 Grams/ACF

LBS/HR = Cs x 0.002205 x Qsd x 60

LBS/HR = 0.0000247x 0.002205 x 8278.5 x 60

LBS/HR = 2.705032E-02

Program Revision:1/16/84

# APPENDIX D-2

## CALCULATED RESULTS FOR CADMIUM AND PARTICULATES

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  2 - 5
( R A W  D A T A )

| | |
|---|---|
| PLANT | : CADMIUM VALIDATION TEST |
| PLANT SITE | : --- , |
| SAMPLING LOCATION | : #1 ESP OUTLET |
| TEST # | : 1-A |
| DATE | : 10/29/85 |
| TEST PERIOD | : 1005-1215 |

| PARAMETER | VALUE |
|---|---|
| Sampling time (min.) | 130 |
| Barometric Pressure (in.Hg) | 30.24 |
| Sampling nozzle diameter (in.) | .248 |
| Meter Volume (cu.ft.) | 66.819 |
| Meter Pressure (in.H2O) | .84 |
| Meter Temperature (F) | 76.7 |
| Stack dimension (sq.in.) | 9424 |
| Stack Static Pressure (in.H2O) | -4 |
| Stack Moisture Collected (gm) | 181.2 |
| Absolute stack pressure(in Hg) | 29.94588 |
| Average stack temperature (F) | 447.9 |
| Percent CO2 | 6.5 |
| Percent O2 | 11.5 |
| Percent N2 | 82 |
| Delps Subroutine result | 19.488 |
| DGM Factor | .9972 |
| Pitot Constant | .84 |

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D S  2 - 5
F I N A L  R E S U L T S

PLANT : CADMIUM VALIDATION TEST
PLANT SITE : --- ,
SAMPLING LOCATION : #1 ESP OUTLET
TEST # : 1-A
DATE : 10/29/85
TEST PERIOD : 1005-1215

| PARAMETER | RESULT |
|---|---|
| Vm(dscf) | 66.3882 |
| Vm(dscm) | 1.880114 |
| Vw gas(scf) | 8.54358 |
| Vw gas (scm) | .2419542 |
| % moisture | 11.40181 |
| Md | .8859819 |
| MWd | 29.5 |
| MW | 28.18879 |
| Vs(fpm) | 2890.058 |
| Vs (mpm) | 881.1151 |
| Flow(acfm) | 189138.2 |
| Flow(acmm) | 5356.394 |
| Flow(dscfm) | 97538.38 |
| Flow(dscmm) | 2762.287 |
| % I | 102.2044 |
| % EA | 113.3228 |

Program Revision:1/16/84

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  5
P A R T I C U L A T E  L O A D I N G

PLANT : CADMIUM VALIDATION TEST
PLANT SITE : --- ,
SAMPLING LOCATION : #1 ESP OUTLET
TEST # : 1-A
DATE : 10/29/85
TEST PERIOD : 1005-1215

| PARAMETER | CADMIUM TOTAL | PARTICULATE TOTAL |
|---|---|---|
| Total Grams | 0.0000605 | 0.0000000 |
| Grams/dscf | 0.0000009 | 0.0000000 |
| Grams/acf | 0.0000005 | 0.0000000 |
| Grains/dscf | 0.0000141 | 0.0000000 |
| Grains/acf | 0.0000073 | 0.0000000 |
| Grams/dscm | 0.0000322 | 0.0000000 |
| Grams/acm | 0.0000166 | 0.0000000 |
| Pounds/dscf | 0.0000000 | 0.0000000 |
| Pounds/acf | 0.0000000 | 0.0000000 |
| Pounds/Hr | 0.0117598 | 0.0000000 |
| Kilograms/Hr | 0.0053342 | 0.0000000 |

* BACK-HALF IMPINGER ANALYSIS WAS NOT REQUIRED

Program Revision:1/16/84

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  2 - 5
( R A W  D A T A )

| | | |
|---|---|---|
| PLANT | : | CADMIUM #2 |
| PLANT SITE | : | |
| SAMPLING LOCATION | : | STACK EXHAUST |
| TEST # | : | CAD 1-A |
| DATE | : | 7/23/86 |
| TEST PERIOD | : | (1605-1651) (1656-1810) |

| PARAMETER | VALUE |
|---|---|
| Sampling time (min.) | 120 |
| Barometric Pressure (in.Hg) | 29.41 |
| Sampling nozzle diameter (in.) | .247 |
| Meter Volume (cu.ft.) | 66.162 |
| Meter Pressure (in.H2O) | .95 |
| Meter Temperature (F) | 124.4 |
| Stack dimension (sq.in.) | 754.7695 |
| Stack Static Pressure (in.H2O) | .05 |
| Stack Moisture Collected (gm) | 170.1 |
| Absolute stack pressure(in Hg) | 29.41368 |
| Average stack temperature (F) | 141.75 |
| Percent CO2 | 5.5 |
| Percent O2 | 15.5 |
| Percent N2 | 79 |
| Delps Subroutine result | 13.88235 |
| DGM Factor | 1.003 |
| Pitot Constant | .84 |

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D S  2 - 5
F I N A L  R E S U L T S

PLANT : CADMIUM #2
PLANT SITE :
SAMPLING LOCATION : STACK EXHAUST
TEST # : CAD 1-A
DATE : 7/23/86
TEST PERIOD : (1605-1651) (1656-1810)

| PARAMETER | RESULT |
|---|---|
| Vm(dscf) | 59.07409 |
| Vm(dscm) | 1.672978 |
| Vw gas(scf) | 8.020215 |
| Vw gas (scm) | .2271325 |
| % moisture | 11.95365 |
| Md | .8804636 |
| MWd | 29.5 |
| MW | 28.12533 |
| Vs(fpm) | 2079.627 |
| Vs (mpm) | 634.0326 |
| Flow(acfm) | 10900.27 |
| Flow(acmm) | 308.6956 |
| Flow(dscfm) | 8278.549 |
| Flow(dscmm) | 234.4485 |
| % I | 93.72329 |
| % EA | 289.3951 |

Program Revision:1/15/84

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D S  2 - 5
F I N A L  R E S U L T S

PLANT : CADMIUM #2
PLANT SITE :
SAMPLING LOCATION : STACK EXHAUST
TEST # : CAD 1-A
DATE : 7/23/86
TEST PERIOD : (1605-1651) (1656-1810)

| PARAMETER | RESULT |
|---|---|
| Vm(dscf) | 59.07409 |
| Vm(dscm) | 1.672978 |
| Vw gas(scf) | 8.020215 |
| Vw gas (scm) | .2271325 |
| % moisture | 11.95365 |
| Md | .8804636 |
| MWd | 29.5 |
| MW | 28.12533 |
| Vs(fpm) | 2079.627 |
| Vs (mpm) | 634.0326 |
| Flow(acfm) | 10900.27 |
| Flow(acmm) | 308.6956 |
| Flow(dscfm) | 8278.549 |
| Flow(dscmm) | 234.4485 |
| % I | 93.72329 |
| % EA | 289.3951 |

Program Revision:1/15/84

R A D I A N  S O U R C E  T E S T
E P A  M E T H O D  5
P A R T I C U L A T E  L O A D I N G

PLANT : CADMIUM #2
PLANT SITE :
SAMPLING LOCATION : STACK EXHAUST
TEST # : CAD 1-A
DATE : 7/23/86
TEST PERIOD : (1605-1651) (1656-1810)

| PARAMETER | PARTICULATE | CADMIUM |
|---|---|---|
| Total Grams | 0.2024000 | 0.0014590 |
| Grams/dscf | 0.0034262 | 0.0000247 |
| Grams/acf | 0.0026021 | 0.0000188 |
| Grains/dscf | 0.0528664 | 0.0003811 |
| Grains/acf | 0.0401510 | 0.0002894 |
| Grams/dscm | 0.1209793 | 0.0008721 |
| Grams/acm | 0.0918815 | 0.0006623 |
| Pounds/dscf | 0.0000076 | 0.0000001 |
| Pounds/acf | 0.0000057 | 0.0000000 |
| Pounds/Hr | 3.7525590 | 0.0270503 |
| Kilograms/Hr | 1.7021500 | 0.0122699 |

Program Revision:1/16/84